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APPLICATIONS OF PHOTOCURABLE  
PRE-CERAMIC POLYMERS

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1        This application is a continuation-in-part of an  
2        application filed June 3, 1999 under Serial No. 09/325,524  
3        and is also a continuation-in-part of the application filed  
4        October 6, 2000 which is a continuation-in-part of an  
5        application filed June 3, 1999 under Serial No. 09/325,524.

6        BACKGROUND OF THE INVENTION

7        The field of the invention is specific applications of  
8        photo curable pre-ceramic polymer chemistry to specific  
9        applications and more particularly to specific applications  
10      such as impregnation and/or coating of ceramic filters for  
11      use in combustion engine exhaust systems.

12       U. S. Patent No. 6,174,565 teaches an abrasion  
13      resistant ceramic material which includes a porous ceramic  
14      material having a surface and a preceramic polymer which is  
15      infiltrated into the surface. The preceramic polymer is

1 converted to a ceramic state.

2 U. S. Patent No. 6,165,240 teaches a filter apparatus  
3 which is for use in a forced air ventilation system. The  
4 filter apparatus has a first fan folded sheet of a washable  
5 first type of filter material, a second fan folded sheet of  
6 a second type of filter material, and fanfolds of the first  
7 and second fan folded sheets are substantially equally shaped  
8 and folded together such that the fanfolds of the first and  
9 second fan folded sheets are interdigitated to form a filter  
10 material assembly. The first type of filter material is  
11 preferably an electrostatically self-charging washable  
12 material such as woven polypropylene and the second type of  
13 filter material is preferably disposable and contains  
14 activated charcoal. The filter material assembly may be  
15 removably disposed in a rectangular filter frame for  
16 mounting the filter material assembly in the forced air  
17 system. The filter frame has at least one crank shaft  
18 rotatably disposed between two opposed side walls which are

1 between an open front end and an open back end of the frame.

2       U. S. Patent No. 4,816,497 teaches a method which is  
3 for the preparation of ceramic materials or articles by the  
4 pyrolysis of mixtures of vinyl- or allyl-containing  
5 preceramic silazane polymers, mercapto compounds, and  
6 photoinitiators. The mixtures are rendered infusible prior  
7 to pyrolysis by ultraviolet (UV) irradiation. This method  
8 is especially suited for the preparation of ceramic fibers.

9       U. S. Patent No. 5,051,215 a rapid method of  
10 infusibilizing (curing) preceramic polymers which includes  
11 treatment the polymers with gaseous nitrogen dioxide. The  
12 infusibilized polymers may be pyrolyzed to temperatures in  
13 excess of about 800° C. to yield ceramic materials with low  
14 oxygen content and, thus, good thermal stability. The  
15 methods are especially useful for the production of ceramic  
16 fibers and, more specifically, to the on-line production of  
17 ceramic fibers.

18       U. S. Patent No. 6,063,327 teaches a method of making a

1 shaped article and composite therefor which includes of a  
2 shaped tool, such as a mold and providing a composite of a  
3 quartz fabric disposed within a polysilazane which is  
4 moldable at a temperature below the curing temperature of  
5 the polysilazane and cured by catalyst. The polysilazane  
6 can be optionally filled with particulate material. A  
7 compaction pressure is applied to the composite to insure  
8 contact of the composite and the tool and prevent loss of  
9 less reactive polysilazane components. The composite is  
10 then cured to hardness by increasing the temperature applied  
11 to the composite at a rate of about 10°C/minute to a  
12 temperature of about 150°C and holding that temperature of  
13 about 150°C up to about 4 hours to provide a cured polymer.  
14 The cured composite is removed from the tool. The polymer  
15 can then be converted to a preceramic by heating the cured  
16 polymer to a temperature sufficiently high in an inert  
17 atmosphere or ammonia gas for a sufficient time. The  
18 removal of carbon will occur when processed in ammonia. The

1 preceramic can then be reprocessed by repeating the above  
2 procedure after cooling and reinfiltrating with uncured  
3 resin.

4 U. S. Patent No. 4,806,612 teaches pre-ceramic  
5 acetylenic polysilanes which contain --(CH(2))<sub>(w)</sub> C.tbd.CR'  
6 groups attached to silicon where w is an integer from 0 to 3  
7 and where R' is hydrogen, an alkyl radical containing 1 to 6  
8 carbon atoms, a phenyl radical, or an --SiR''(3) radical  
9 wherein R'' is an alkyl radical containing 1 to 4 carbon  
10 atoms. The acetylenic polysilanes are prepared by reacting  
11 chlorine-or bromine-containing polysilanes with either a  
12 Grignard reagent of general formula R'C.tbd.C(CH(2))<sub>(w)</sub> MgX'  
13 where w is an integer from 0 to 3 and X' is chlorine,  
14 bromine, or iodine or an organolithium compound of general  
15 formula R'C.tbd.C(CH(2))<sub>(w)</sub> Li where w is an integer from 0  
16 to 3. The acetylenic polysilanes can be converted to  
17 ceramic materials by pyrolysis at elevated temperatures  
18 under an inert atmosphere.

1        U. S. Patent No. 4,800,211 teaches 3-Hydroxybenzo[b]  
2        thiophene-2-carboxamide derivatives which have been prepared  
3        by: (1) treating a substituted 2-halobenzoate with a  
4        thioacetamide; (2) treating a substituted thiosalicylate  
5        with an appropriately substituted haloacetamide; and (3)  
6        further synthetic modification of compounds prepared above.

7        These compounds have been found to be effective inhibitors  
8        of both cyclooxygenase and lipoxygenase and thereby useful  
9        in the treatment of pain, fever, inflammation, arthritic  
10      conditions, asthma, allergic disorders, skin diseases,  
11      cardiovascular disorders, psoriasis, inflammatory bowel  
12      disease, glaucoma or other prostaglandins and/or leukotriene  
13      mediated diseases.

14       U. S. Patent 4,588,832 teaches a novel and economical  
15      route for the synthetic preparation of a 1-alkynyl  
16      trihydrocarbyl silane compound. The method includes the  
17      steps of reacting metallic sodium with a hydrocarbyl-  
18      substituted acetylene or allene compound to form a

1 substituted sodium acetylide and reacting the acetylide with  
2 a trihydrocarbyl monohalogenosilane in the reaction mixture  
3 which is admixed with a polar organic solvent such as  
4 dimethylformamide.

5 U. S. Patent No. 4,505,726 teaches an exhaust gas  
6 cleaning device provided with a filter member which collects  
7 carbon particulates in exhaust gases discharged from a  
8 diesel engine and an electric heater for burning off the  
9 particulates collected by the filter member. The filter  
10 member is composed of a large number of intersecting porous  
11 walls which define a large number of inlet gas passages and  
12 outlet gas passages which are adjacent to each other. The  
13 electric heater is composed of at least one film-shaped  
14 heating resistor which is directly formed on the upstream  
15 end surface of the filter member so as to be integral  
16 therewith. When the amount of carbon particulates collected  
17 by the filter member reaches a predetermined level, electric  
18 current is supplied to the electric heater. The carbon

1   particulates adhered to the upstream end surface of the  
2   filter member are ignited and burnt off. Then, the  
3   combustion of carbon particulates spreads to the other  
4   carbon particulates collected in the other portion of the  
5   filter member.

6       U. S. Patent No. 5,843,304 teaches a materials  
7   treatment system which includes filtration and treatment of  
8   solid and liquid components of a material, such as a waste  
9   material. A filter or substrate assembly is provided which  
10   allows liquids to pass therethrough, while retaining solids.  
11   The solids are then incinerated utilizing microwave energy,  
12   and the liquids can be treated after passing through the  
13   filter element, for example, utilizing a treatment liquid  
14   such as an oxidant liquid. The filter assembly can also  
15   include an exhaust filter assembly which removes solids or  
16   particulate matter from exhaust gasses, with the retained  
17   solids/particulates incinerated utilizing microwave energy.

18       U. S. Patent No. 5,074,112 teaches a filter assembly

for an internal combustion engine which includes, in combination, a housing defining an exhaust gas passage having an inlet end and an outlet end and a cavity intermediate the inlet and outlet ends thereof and in serial fluid communication therewith, the cavity defining an electromagnetically resonant coaxial line waveguide, a filter disposed within the cavity for removing particulate products of combustion from exhaust gases passing through the cavity, and a mechanism for producing axisymmetrically distributed, standing electromagnetic waves within the cavity whereby to couple electromagnetic energy in the waves into lossy material in the cavity to produce heat for incinerating the particulate products of combustion accumulated on the filter.

U. S. Patent No. 4,934,141 teaches a device for microwave elimination of particles contained in the exhaust gases of diesel engines in which a microwave source and a conductor of the electromagnetic field generated by the

1 source is joined with a resonator mounted on an element of  
2 the pipe for the exhaust gases which contains an insert,  
3 characterized by the fact that the insert consists of a  
4 filter whose upstream and downstream ends are offset toward  
5 the inside of the cavity defined by the resonator and  
6 delimit two chambers in which conductors of the electro-  
7 magnetic field come out, respectively.

8 U. S. Patent No. 4,825,651 teaches a device and method  
9 for separating soot or other impurities from the exhaust  
10 gases of an internal-combustion engine, particularly a  
11 diesel internal-combustion engine, comprises a microwave  
12 source that is coupled to the intermediate section of the  
13 exhaust pipe that is constructed for the development  
14 of an electromagnetic field, an effective burning of the  
15 soot with a low flow resistance, the intermediate section  
16 being developed as a cavity resonator and at its exhaust gas  
17 inlet and exhaust gas outlet, is equipped with a metal grid,  
18 and an insert made of a dielectric material in the cavity

1 resonator concentrates the exhaust gas flow in the area of  
2 high energy density of the electromagnetic field.  
3 U. S. Patent No. 4,477,771 teaches conductive  
4 particulates in the form of soot which are collected from  
5 diesel engine exhaust gases on a porous wall monolithic  
6 ceramic filter in such a way that the soot is somewhat  
7 uniformly distributed throughout the filter. The filter is  
8 housed in a chamber having a property of a microwave  
9 resonant cavity and the cavity is excited with microwave  
10 energy. As the particulates are collected the cavity appears  
11 to the microwaves to have an increasing dielectric constant  
12 even though the matter being accumulated is conductive  
13 rather than dielectric so that as collected on the porous  
14 filter it has the property of an artificial dielectric. The  
15 response of the cavity to the microwave energy is monitored  
16 to sense the effect of the dielectric constant of the  
17 material within the cavity to provide a measure of the soot  
18 content in the filter.

1        U. S. Patent No. 5,902,514 teaches a material for  
2 microwave band devices which are used by the general people  
3 and in industrial electronic apparatuses. Particularly, a  
4 magnetic ceramic composition for use in microwave devices, a  
5 magnetic ceramics for use in microwave devices and a  
6 preparation method therefore are disclosed, in which the  
7 saturation magnetization can be easily controlled, and a low  
8 ferri-magnetic resonance half line width and an acceptable  
9 curie temperature are ensured. The magnetic ceramic  
10 composition for microwave devices includes yttrium oxide  
11 ( $\text{Y}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), tin oxide ( $\text{SnO}_2$ )),  
12 aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and a calcium supply source.  
13 The magnetic ceramics for the microwave devices are  
14 manufactured by carrying out a forming and a sintering after  
15 mixing: yttrium oxide, iron oxide, tin oxide, aluminum oxide  
16 and calcium carbonate (or calcium oxide) based on a formula  
17 shown below. It has a saturation magnetization of 100-1,800  
18 G at the normal temperature, a temperature coefficient for

1 the saturation magnetization of 0.2%/ $^{\circ}$  C, and a ferri-  
2 magnetic resonance half line width of less than 60 Oe, Y(3-  
3 x) Ca(x/2) Sn(x/2) Fe(5-y) Al(y) O(12) where 0.1<=x<=1, and  
4 0.1<=y<=1.5.

5 U. S. Patent No. 5,843,860 teaches a ceramic  
6 composition for high-frequency dielectrics which includes  
7 the main ingredients of ZrO(2), SnO(2) and TiO(2) and a  
8 subsidiary ingredient of (Mn(NO(3))(2).4H(2) O). A  
9 homogeneous ceramic composition can be prepared by a process  
10 which comprises the steps of: adding ZrO(2), SnO(2) and  
11 TiO(2) by the molar ratio to satisfy (ZrO(2))(1-x)  
12 (SnO(2))(x) (TiO(2))(1+y) (wherein, 0.1M  $^{\circ}$  C or above; and,  
13 adding 1% or less of Mn(NO(3))(2).4H(2) O by weight of  
14 MnO to the mixture. The ceramic composition of the  
15 invention has a high dielectric constant of 40 or more, a  
16 quality factor of 7000 or more, and a temperature  
17 coefficient of resonance frequency below 10. Accordingly,  
18 it can be used for an integrated circuit at microwave as

1 well as at high frequency, or for dielectric resonators.

2 U. S. Patent No. 5,808,282 teaches a microwave  
3 susceptor bed which is useful for sintering ceramics,  
4 ceramic composites and metal powders. The microwave  
5 susceptor bed contains granules of a major amount of a  
6 microwave susceptor material, and a minor amount of a  
7 refractory parting agent, either dispersed in the susceptor  
8 material, or as a coating on the susceptor material.

9 Alumina is the preferred susceptor material. Carbon is the  
10 most preferred parting agent. A sintering process uses the  
11 bed to produce novel silicon nitride products.

12 U. S. Patent No. 5,446,270 teaches a composition which  
13 includes susceptors having the capability of absorbing  
14 microwave energy and a matrix. The susceptors includes a  
15 particulate substrate substantially non-reflective of  
16 microwave energy and a coating capable of absorbing  
17 microwave energy. The matrix is substantially non-  
18 reflective of microwave energy. Susceptors are typically

1 particles having a thin-film coating thereon. The matrix  
2 typically includes polymeric or ceramic materials that are  
3 stable at temperatures conventionally used in microwave  
4 cooking. The composition allows reuse of the susceptors,  
5 eliminates decline in heating rate, eliminates arcing,  
6 allows the heating rate to be controlled, allows overheating  
7 to be controlled, and allows formation of microwave heatable  
8 composite materials having very low metal content.

9       U. S. Patent No. 5,365,042 teaches a heat treatment  
10 installation for parts made of a composite material which  
11 has a ceramic matrix and which includes a treatment  
12 enclosure. The treatment enclosure is connected to a  
13 microwave generator by a wave-guide and which includes a  
14 press for hot pressing a part to be treated in the enclosure  
15 and a gas source for introducing a protective gas into the  
16 enclosure.

17       U. S. Patent No. 5,126,529 teaches a method for forming  
18 a three-dimensional object by thermal spraying which

1 utilizes a plurality of masks positioned and removed over a  
2 work surface in accordance with a predetermined sequence.  
3 The masks correspond to cross sections normal to a  
4 centerline through the work-piece. One set of masks defines  
5 all cross sections through the work-piece. A second set of  
6 masks contains at least one mask. The mask corresponds to  
7 each mask of the first set. Masks from each set are  
8 alternatively placed above a work surface and sprayed with  
9 either a deposition material from which the work-piece will  
10 be made or a complementary material. In this manner, layers  
11 of material form a block of deposition material and  
12 complementary material. The complementary material serves  
13 as a support structure during forming and is removed.  
14 Preferably, the complementary material has a lower melting  
15 temperature than the deposition material and is removed by  
16 heating the block. Alternatively, one could mask only for  
17 the deposition material and remove complementary material  
18 overlying the deposition material after each spraying of

1 complementary material.

2       U. S. Patent No. 4,199,387 teaches an air filter unit  
3 of the pleated media, high efficiency type. The media pleat  
4 edges are sealed to the supporting frame to prevent bypass  
5 of air with a ceramic adhesive and fibrous ceramic mat which  
6 allows the unit to be exposed to high temperatures (e.g., up  
7 to 2000° F.) without danger of seal breakdown. While in the  
8 form of a slurry the adhesive is applied, for example, with  
9 a trowel to the zig-zag pleated edges of the media which,  
10 together with corrugated spacers, forms the filter core.  
11 The latter is then surrounded on four sides by the  
12 compressible mat of fibrous ceramic material and inserted in  
13 a box-like support frame with the slurry filling the space  
14 between the pleated edges of the media and the fibrous mat.  
15 The filter core and the surrounding mat are assembled with  
16 the support frame while the slurry is still wet whereby,  
17 upon hardening, the resulting layers of ceramic cement  
18 provide a complete, heat-resistant seal while avoiding

1 cracking in normal handling due to the resilience of the  
2 compressed fibrous mat which maintains an airtight seal  
3 between hardened ceramic and support frame.

4 U. S. Patent No. 6,063,150 teaches a self-cleaning  
5 particle filter for Diesel engines which includes a filter  
6 housing, control circuitry, a removable filter sandwich and  
7 independent power source. The removable filter sandwich  
8 includes a number of sintered metal strips sewn and  
9 positioned between two sheets of inorganic material to  
10 provide a filter sandwich. Current is delivered to the  
11 metal filter strips to efficiently burn off carbon, lube oil  
12 and unburned fuel particulates which have been filtered from  
13 exhaust gas. The filter sandwich is formed into a  
14 cylindrical configuration and mounted onto a perforated  
15 metal carrier tube for receiving and filtering exhaust gas.

16 U. S. Patent No. 6,101,793 teaches an exhaust gas  
17 filter having a ceramic filter body is configured such that  
18 a specific heat  $h$  (cal/g °C) of ceramic powder constituting

1 the body, an a bulk specific gravity  $d$  ( $\text{g}/\text{cm}(\wedge 3)$ ) of the  
2 filter, satisfy the relation  $0.12$  ( $\text{cal}/\text{cm}(\wedge 3)$   $^{\circ}\text{C}$ )  
3  $\leq h \cdot d \leq 0.19$  ( $\text{cal}/\text{cm}(\wedge 3)$   $^{\circ}\text{C}$ ). The ceramic filter body  
4 includes a plurality of cells which extend axially to open  
5 at opposite ends of the body. One of the opposite axial  
6 ends of each of the cells is closed by a filler in such a  
7 manner that the closed ends of the cells and the open ends  
8 of the cells are arranged in an alternating configuration.  
9 The filter traps particulates in the exhaust gas, and the  
10 trapped particulates are removed by regeneration combustion  
11 of the filter. The filter exhibits excellent durability,  
12 thus preventing the formation of cracks in the surface and  
13 interior of the filter. When the filter is mounted on a  
14 diesel engine, the diesel engine advantageously does not  
15 discharge black smoke.

16 U. S. Patent No. 5,756,412 teaches a dielectric ceramic  
17 composition for microwave applications which consists  
18 essentially of the compound having a formula  $B'B(2) "O(6)$ ,

1 wherein B' is at least one metal selected from the group of  
2 Mg, Ca, Co, Mn, Ni and Zn, and wherein B" is one of Nb or Ta,  
3 and additionally includes at least one compound selected  
4 from the group of CuO, V(2) O(5), La(2) O(3), Sb(2) O(5),  
5 WO(3), MnCO(3), MgO, SrCO(3), ZNO, and Bi(2) O(3) as an  
6 additive, wherein the amount of the additive is 0.05% to  
7 2.0% by weight of the total weight of the composition.

8         The synthesis of polycarbosilane from the pyrolytic  
9 condensation reaction of polydimethylsilane obtained from  
10 the reaction of dichlorodimethylsilane with an alkali metal,  
11 such as sodium. In the latter approach, polydimethylsilane  
12 can be prepared by Wurtz type coupling of dichlorodimethyl-  
13 silane with sodium in toluene. The direct pyrolysis of  
14 polydimethylsilane, a viscous thermoplastic resin, at high  
15 temperature gives SiC in a ceramic yield of about 30%-40%.  
16 By thermally cross-linking the polydimethylsilane into an  
17 infusible rigid thermoset polymer, which is insoluble in any  
18 common solvents, the subsequent pyrolysis yield is on the

1 order of 88%-93%. This thermolysis was accomplished by  
2 refluxing the polydimethyl-silane to in excess of 350°C.

3 Numerous pre-ceramic polymers with improved yields of  
4 the ceramic have been described in U. S. Patent No.  
5 5,138,080, U. S. Patent No. 5,091,271, U. S. Patent No.  
6 5,051,215 and U. S. Patent No. 5,707,471. The fundamental  
7 chemistry contained in these embodiments is specific to the  
8 process employed and mainly leaves the pre-ceramic polymer  
9 in a thermoplastic state. These pre-ceramic polymers which  
10 catalytic or photo-induced cross-linking do not satisfy the  
11 high ceramic yield, purity and fluidity in combination with  
12 low temperature crosslinking ability necessary for producing  
13 large densified ceramic structures in a single step  
14 continuous process.

15 U. S. Patent No. 5,138,080 teaches a novel polysila-  
16 methylenosilane polymers which has polysilane-poly-  
17 carbosilane skeleton which can be prepared in one-step  
18 reaction from mixtures of chlorosilaalkanes and organochloro

1 silanes with alkali metals in one of appropriate solvents or  
2 in combination of solvents thereof. Such polysilamethyleno  
3 silane polymers are soluble and thermoplastic and can be  
4 pyrolyzed to obtain improved yields of silicon carbide at  
5 atmospheric pressure.

6 U. S. Patent No. 5,091,271 teaches a shaped silicon  
7 carbide-based ceramic article which has a mechanical  
8 strength which is produced at a high efficiency by a process  
9 including the step of forming an organic silicone polymer,  
10 for example, polycarbosilastyrene copolymer, into a  
11 predetermined shape, for example, a filament or film; doping  
12 the shaped polymer with a doping material consisting of at  
13 least one type of halogen, for example, bromine or iodine,  
14 in an amount of 0.01% to 150% based on the weight of the  
15 shaped polymer, to render the shaped polymer infusible; and  
16 pyrolyzing the infusible shaped polymer into a shaped SiC-  
17 based ceramic article at a temperature of 800° C to 1400° C  
18 in an inert gas atmosphere, optionally the halogen-doped

1 shaped polymer being treated with a basic material, for  
2 example, ammonia, before the pyrolyzing step, to make the  
3 filament uniformly infusible.

4 U. S. Patent No. 5,300,605 teaches poly(I-hydro-1-R-1-  
5 silapent-3-ene) homopolymers and copolymers which contain  
6 silane segments with reactive silicon-hydride bonds and  
7 contain hydrocarbon segments with cis and trans carbon-  
8 carbon double bonds.

9 U. S. Patent No. 5,171,810 teaches random or block  
10 copolymers with (I-hydro-I-R-I-sila-cis-pent-3-ene), poly(I-  
11 hydro-1-R-3,4 benzo-1-sila pent-3-ene) and disubstituted I-  
12 silapent-3-ene repeating units of the general formula ##STR1##  
13 where R is hydrogen, an alkyl radical containing from one to  
14 four carbon atoms or phenyl, R.<sup>1</sup> is hydrogen, an alkyl  
15 radical containing from one to four carbon atoms, phenyl or a  
16 halogen and R.<sup>2</sup> is hydrogen, or R.<sup>1</sup> and R.<sup>2</sup> are  
17 combined to form a phenyl ring, are prepared by the anionic  
18 ring opening polymerization of silacyclopent-3-enes or 2-

1 silaindans with an organometallic base and cation coordinating  
2 ligand catalyst system or a metathesis ring opening catalyst  
3 system.

4 U. S. Patent No. 5,169,916 Poly(I -hydro- I -R- I -  
5 sila-cis-pent-3-ene) and poly(I -hydro- I -R-3,4 benzo-1-  
6 sila pent-3-ene) polymers which has repeating units of the  
7 general formula polycarbosilane containing at least two  
8 tbd.SiH groups per molecule via intimately contacting such  
9 fusible polycarbosilane with an effective hardening amount  
10 of the vapors of sulfur.

11 U. S. Patent No. 5,064,915 teaches insoluble poly-  
12 carbosilanes, readily pyrolyzed into silicon carbide ceramic  
13 materials such as SiC fibers, are produced by hardening a  
14 fusible polycarbosilane containing at least two tbd. SiH  
15 groups per molecule via intimately contacting such fusible  
16 polycarbosilane with an effective hardening amount of the  
17 vapors of sulfur.

1        U. S. Patent No. 5,049,529 teaches carbon nitride ceramic  
2 materials which are produced by hardening a fusible  
3 polycarbosilane containing at least two tbd.SiH groups per  
4 molecule by intimately contacting such fusible polycarbosilane  
5 with an effective hardening amount of the vapors of sulfur,  
6 next, heat treating the infusible polycarbosilane which  
7 results under an ammonia atmosphere to such extent as to  
8 introduce nitrogen into the infusible polycarbosilane without  
9 completely removing the carbon therefrom and then heat  
10 treating the nitrogenated polycarbosilane in a vacuum or in an  
11 inert atmosphere to such extent as to essentially completely  
12 convert it into a ceramic silicon carbon nitride.

13       U. S. Patent No. 5,051,215 teaches a rapid method of  
14 infusibilizing pre-ceramic polymers which includes treatment  
15 of the polymers with gaseous nitrogen dioxide. The  
16 infusibilized polymers may be pyrolyzed to temperatures in  
17 excess of about 800°C to yield ceramic materials with low  
18 oxygen content and, thus, good thermal stability. The methods

1 are especially useful for the production of ceramic fibers  
2 and, more specifically, to the on-line production of ceramic  
3 fibers.

4 U. S. Patent No. 5,028,571 teaches silicon nitride  
5 ceramic materials which are produced by hardening a fusible  
6 polycarbosilane containing at least two dbd.SiH groups per  
7 molecule by intimately contacting such fusible polycarbo-  
8 silane with an effective hardening amount of the vapors of  
9 sulfur and then pyrolyzing the infusible polycarbosilane  
10 which results under an ammonia atmosphere.

11 U. S. Patent No. 4,847,027 teaches a method for the  
12 preparation of ceramic materials or articles by the pyrolysis  
13 of pre-ceramic polymers wherein the pre-ceramic polymers are  
14 rendered infusible prior to pyrolysis by exposure to gaseous  
15 nitric oxide. Ceramic materials with low oxygen content,  
16 excellent physical properties, and good thermal stability can  
17 be obtained by the practice of this process. This method is  
18 especially suited for the preparation of ceramic fibers.

1       U.S. Patent No. 5,714,025 teaches a method for preparing  
2       a ceramic-forming pre-preg tape which includes the steps of  
3       dispersing in water a ceramic-forming powder and a fiber,  
4       flocculating the dispersion by adding a cationic wet strength  
5       resin and an anionic polymer, dewatering the flocculated  
6       dispersion to form a sheet, wet pressing and drying the sheet,  
7       and coating or impregnating the sheet with an adhesive  
8       selected from the group consisting of a polymeric ceramic  
9       precursor, and a dispersion of an organic binder and the  
10      materials used to form the sheet. The tape can be used to  
11      form laminates, which are fired to consolidate the tapes to a  
12      ceramic.

13       U. S. Patent No. 5,707,471 teaches a method for preparing  
14       fiber reinforced ceramic matrix composites which includes the  
15       steps of coating refractory fibers, forming the coated fibers  
16       into the desired curing the coated fibers to form a pre-preg,  
17       heating the pre-preg to form a composite and heating the  
18       composite in an oxidizing shape, environment to form an in

1   situ sealant oxide coating on the composite. The refractory  
2   fibers have a interfacial coating thereon with a curable pre-  
3   ceramic polymer which has a char containing greater than about  
4   50% sealant oxide atoms. The resultant composites have good  
5   oxidation resistance at high temperature as well as good  
6   strength and toughness.

7       U. S. Patent No. 5,512,351 teaches a new pre-preg  
8   material which has good tack drape properties and feasible  
9   out-time. The pre-preg material is prepared by impregnating  
10   inorganic fibers with a composition which includes a fine  
11   powder of a metal oxide or oxides having an average particle  
12   diameter of not larger than one micrometer, a soluble  
13   siloxane polymer having double chain structure, a  
14   trifunctional silane compound having at least one  
15   ethylenically unsaturated double bond in the molecule  
16   thereof, a organic peroxide and a radically polymerizable  
17   monomer having at least two ethylenically unsaturated double  
18   bonds and heating the impregnated fibers.

1       U. S. Patent No. 4,835,238 teaches a reaction of 1,1-  
2 dichloro-silacyclobutanes with nitrogen-containing  
3 difunctional nucleophiles which gives polysilacyclobuta-  
4 silazanes which can be crosslinked and also converted to  
5 ceramic materials.

6       Numerous processing mechanics with various direct  
7 applications have been described, for example, in the U. S.  
8 Patent No. 5,820,483, U. S. Patent No. 5,626,707, U. S.  
9 Patent No. 5,732,743 and U. S. Patent No. 5,698,055. The  
10 process mechanics are for a single product process and do  
11 not permit continuous curing and pyrolysis in a single step  
12 to produce highly dense thick ceramic components.

13      U. S. Patent No. 5,820,483 teaches methods for  
14 manufacturing a shaft for a golf club. A plug is detachably  
15 affixed to a distal end of a mandrel. A plurality of plies  
16 of pre-preg composite sheet are wrapped around the mandrel  
17 and plug and, thereafter, heated causing the resin  
18 comprising the various plies to be cured. The mandrel is

1 then removed from the formed shaft, leaving the plug as an  
2 integral part of the distal tip of the shaft.

3 U. S. Patent No. 5,626,707 teaches an apparatus which  
4 produces a composite tubular article. The apparatus includes  
5 a frame, a drive mechanism for rotating a mandrel, at least  
6 two spindles mounted to the frame, a tensioner and a belt  
7 extending between the first and second spindles. The  
8 apparatus may be used to roll pre-preg strips or similar  
9 sheets of composite materials around the mandrel. The belt  
10 travels over the spindles, and the spindles guide the belt  
11 through changes in its direction of travel. The mandrel is  
12 mounted in the drive mechanism in contact with the belt, which  
13 changes its direction of travel around the mandrel. The lower  
14 surface of the belt bears against upper portions of the  
15 spindles, and the mandrel contacts the upper surface of the  
16 belt. As the drive mechanism rotates the mandrel, pre-preg  
17 sheets are fed between the mandrel and the belt and are  
18 thereby wrapped around the mandrel. The belt presses the pre-

1 preg sheets against the mandrel. The wrapped mandrel may then  
2 be removed from the apparatus and cured in any suitable manner  
3 known in the art to produce the a composite tubular article.

4 U. S. Patent No. 5,732,743 teaches a method for joining  
5 and repairing pipes includes the step of utilizing photo-  
6 curable resins in the form of a fabric patch to for quickly  
7 repairing or sealing pipes. A photo-curable flexible pre-preg  
8 fabric is wrapped over the entire area of the pipe to be  
9 joined or repaired. The pre-preg fabric contains multiple  
10 layers of varying widths and lengths. The pre-preg fabric is  
11 then exposed to photo-radiation which cures and seals the  
12 pipe.

13 U. S. Patent No. 5,698,055 teaches a method for making a  
14 reinforced tubular laminate. A dry braided fiber sleeve is  
15 placed between a mandrel and spiral tape wrap either over,  
16 under, or layered with a pre-preg material. During the  
17 initial stages of the curing process, while the temperature is  
18 rising, the resin in the pre-preg material flows and wets out

1 the dry braid. When the final cure takes place, the braid  
2 becomes an integral part of the finished laminate. The choice  
3 of fiber materials and braid angle permits various tubular  
4 laminate strengths. The selection of fiber colors and  
5 patterns permit a wide variety of tubular laminate aesthetic  
6 characteristics.

7 U. S. Patent No. 5,632,834 teaches sandwich structures  
8 which are made of fiber-reinforced ceramics. The base  
9 substance of the ceramic matrix consists of a Si-organic  
10 polymer and a ceramic or metallic powder. A cross-linking of  
11 the Si-organic polymer takes place under increased pressure  
12 and at an increased temperature. After the joining of the  
13 facings and the honeycomb core, the sandwich structure is  
14 pyrolysed to form a ceramic material

15 U. S. Patent No. 5,641,817 teaches organometallic ceramic  
16 precursor binders which are used to fabricate shaped bodies by  
17 different techniques. Exemplary shape making techniques which  
18 utilize hardenable, liquid, organometallic, ceramic precursor

1 binders include the fabrication of negatives of parts to be  
2 made (e.g., sand molds and sand cores for metalcasting, etc.),  
3 as well as utilizing ceramic precursor binders to make shapes  
4 directly (e.g., brake shoes, brake pads, clutch parts,  
5 grinding wheels, polymer concrete, refractory patches and  
6 liners, etc.). A thermosettable, liquid ceramic precursors  
7 provides suitable-strength sand molds and sand cores at very  
8 low binder levels and, upon exposure to molten metal casting  
9 exhibit low emissions toxicity as a result of their high char  
10 yields of ceramic upon exposure to heat. The process involves  
11 the fabrication of preforms used in the formation of composite  
12 articles. Production costs, and relatively poor physical  
13 properties prohibits their inherently large cost of  
14 capitalization, high wide use.

15 U. S. Patent No. 4,631,179 teaches this ring-opening-  
16 polymerization reactions method to obtain a linear polymer  
17 of the formula [SiH<sub>2</sub>CH<sub>2</sub>]<sub>n</sub>. This polymer  
18 exhibit ceramics yields up to 85% on pyrolysis. The

1 starting material for the ring-opening-polymerization  
2 reaction was the cyclic compound [SiH.<sub>2</sub> CH.<sub>2</sub>  
3 ].<sub>2</sub>, which is difficult and costly to obtain in pure  
4 form by either of the procedures that have been reported.

5 U. S. Patent No. 5,888,641 teaches an exhaust manifold  
6 for an engine which are made of all fiber reinforced ceramic  
7 matrix composite material so as to be light weight and high  
8 temperature resistant. A method of making the exhaust  
9 manifold includes the steps of forming a liner of a cast  
10 monolithic ceramic material containing pores, filling the  
11 pores of the cast monolithic ceramic material with a pre-  
12 ceramic polymer resin, coating reinforcing fibers with an  
13 interface material to prevent a pre-ceramic polymer resin  
14 from adhering strongly to the reinforcing fibers, forming a  
15 mixture of a pre-ceramic polymer resin and reinforcing  
16 fibers coated with the interface material, forming an  
17 exhaust manifold shaped structure from the mixture of the  
18 pre-ceramic polymer resin and the reinforcing fibers coated

1 with the interface material by placing the mixture on at  
2 least a portion of the cast monolithic ceramic material,  
3 and firing the exhaust component shaped structure at a  
4 temperature and a time sufficient to convert the pre-ceramic  
5 polymer resin to a ceramic thereby forming a reinforced  
6 ceramic composite.

7 U. S. Patent No. 5,153,295 teaches compositions of  
8 matter which have potential utility as precursors to silicon  
9 carbide. These compositions are obtained by a Grignard  
10 coupling process starting from chlorocarbosilanes, a readily  
11 available class of compounds. The new precursors  
12 constitute a fundamentally new type of polycarbosilane that  
13 is characterized by a branched,  $[Si--C]_{\cdot sub \cdot n}$  "backbone"  
14 which consists of  $SiR_{\cdot sub \cdot 3} CH_{\cdot sub \cdot 2} --$ ,  $--SiR_{\cdot sub \cdot 2} CH_{\cdot sub \cdot 2} --$ ,  
15  $.dbd.SiRCH_{\cdot sub \cdot 2} --$ , and  $.tbd.SiCH_{\cdot sub \cdot 2} --$   
16 units (where R is usually H but can also be other organic  
17 or inorganic groups, e.g., lower alkyl or alkenyl, as may be  
18 needed to promote crosslinking or to modify the physical

1 properties of the polymer or the composition of the final  
2 ceramic product). A key feature of these polymers is that  
3 substantially all of the linkages between the Si--C units  
4 are "head-to-tail", i.e., they are Si to C. The  
5 polycarbosilane "SiH<sub>2</sub> CH<sub>2</sub>" has a carbon to  
6 silicon ratio of 1 to 1 and where substantially all of the  
7 substituents on the polymer backbone are hydrogen. This  
8 polymer consists largely of a combination of the four  
9 polymer "units": SiH<sub>3</sub> CH<sub>2</sub>--, --SiH<sub>2</sub> CH<sub>2</sub>--  
10 --, .dbd.SiHCH<sub>2</sub>--, and .tbd.SiCH<sub>2</sub>-- which are  
11 connected "head-to-tail" in such a manner that a complex,  
12 branched structure results. The branched sites introduced  
13 by the last two "units" are offset by a corresponding number  
14 of SiH<sub>3</sub> CH<sub>2</sub>-- "end groups" while maintaining the  
15 alternating Si--C "backbone". The relative numbers of the  
16 polymer "units" are such that the "average" formula is  
17 SiH<sub>2</sub> CH<sub>2</sub>. These polymers have the advantage that  
18 it is only necessary to lose hydrogen during pyrolysis, thus

1 ceramic yields of over 90% are possible, in principle. The  
2 extensive Si--H functionality allows facile crosslinking and  
3 the 1 to 1 carbon to silicon ratio and avoids the  
4 incorporation of excess carbon in the SiC products that are  
5 ultimately formed. The synthetic procedure employed to make  
6 them allows facile modification of the polymer, such as by  
7 introduction of small amounts of pendant vinyl groups, prior  
8 to reduction. The resulting vinyl-substituted "SiH<sub>2</sub>  
9 CH<sub>2</sub>" polymer has been found to have improved  
10 crosslinking properties and higher ceramic yield.

11 A pre-ceramic polymer is prepared by a thermally  
12 induced methylene insertion reaction of polydimethylsilane.  
13 The resulting polymer is only approximately represented by  
14 the formula [SiHMeCH<sub>2</sub>]<sub>n</sub>, as significant amounts  
15 of unreacted (SiMe<sub>2</sub>)<sub>n</sub> units, complex rearrange-  
16 ments, and branching are observed. Neither the preparation  
17 nor the resulting structure of this precursor are therefore  
18 similar to the instant process. In addition to the

1 carbosilane "units", large amounts of Si--Si bonding remains  
2 in the "backbone" of the polymer. This polymer, in contrast  
3 to the instant process, contains twice the stoichiometric  
4 amount of carbon for SiC formation. The excess carbon must  
5 be eliminated through pyrolytic processes that are by no  
6 means quantitative. Despite the shortcomings, this polymer  
7 has been employed to prepare "SiC" fiber. However, it must  
8 be treated with various crosslinking agents prior to  
9 pyrolysis which introduce contaminants. This results in a  
10 final ceramic product that contains significant amounts of  
11 excess carbon and silica which greatly degrade the high  
12 temperature performance of the fiber.

13 SiC precursors predominately linear polycarbo-silanes  
14 have been prepared via potassium dechlorination of chloro-  
15 chloromethyl-dimethylsilane. The resulting polymers have  
16 not been fully characterized, but probably contain  
17 significant numbers of Si--Si and CH<sub>2</sub>--CH<sub>2</sub> groups  
18 in the polymer backbone. The alkali metal dechlorination

1 process used in the synthesis of such materials does not  
2 exhibit the selective head-tail coupling found with Grignard  
3 coupling. The pendant methyl groups in such materials also  
4 lead to the incorporation of excess carbon into the system.  
5 In several polymer systems mixtures containing vinylchloro-  
6 silanes (such as CH<sub>2</sub>.dbd.CH--Si(Me)Cl<sub>2</sub>) and  
7 Me<sub>2</sub>SiCl<sub>2</sub> are coupled by dechlorination with  
8 potassium in tetrahydro-furan. U. S. Patent No. 4,414,403  
9 and U. S. Patent No. 4,472,591 both teach this method. The  
10 "backbone" of the resulting polymers consists of a  
11 combination of Si--Si and Si--CH<sub>2</sub>CH(--Si)<sub>2</sub> units.  
12 Later versions of this polymer Me(H)SiCl<sub>2</sub> in addition  
13 to the Me<sub>2</sub>SiCl<sub>2</sub> and are subjected to a sodium-  
14 hydrocarbon dechlorination process which does not attack  
15 vinyl groups. The resulting polymer consists of a  
16 predominately linear, Si--Si "backbone" bearing pendant  
17 methyl groups, with some Si--H and Si--CH<sub>2</sub>dbd.CH<sub>2</sub>  
18 functionality to allow crosslinking on pyrolysis.

1        None of these precursors derived using vinylchloro-  
2        silanes are similar to those of the process in that having  
3        predominantly Si--Si bonded "backbones", they are  
4        essentially polysilanes, not polycarbosilanes. In addition,  
5        the carbon in these polymers is primarily in the form of  
6        pendant methyl functionality and is present in considerable  
7        excess of the desirable 1 to 1 ratio with silicon. The  
8        ceramic products obtained from these polymers are known to  
9        contain considerable amounts of excess carbon.

10        Polymeric precursors to SiC have been obtained by  
11        redistribution reactions of methyl-chloro-disilane  
12        ( $\text{Me}_{\text{sub.}6-\text{x}} \text{Cl}_{\text{sub.}x} \text{Si}_{\text{sub.}2}$ ,  $x=2-4$ ) mixtures, catalyzed by  
13        tetraalkyl-phosphonium halides which U. S. Patent No.  
14        4,310,481, U. S. Patent No. 4,310,482 and U. S. Patent No.  
15        4,472,591 teach. In a typical preparation, elemental  
16        analysis of the polymer was employed to suggest the  
17        approximate formula  $[\text{Si}(\text{Me})_{\text{sub.}1.15} (\text{H})_{\text{sub.}0.25}]_{\text{sub.}n}$ ,  
18        with n averaging about 20. The reaction is fundamentally

1 different than that involved in the process and the  
2 structures of the polymers are also entirely different,  
3 involving what is reported to be a complex arrangement of  
4 fused polysilane rings with methyl substitution and a  
5 polysilane backbone.

6 The formation of carbosilane polymers with pendent  
7 methyl groups as by-products of the "reverse-Grignard"  
8 reaction of chloromethyl-dichloro-methylsilane. The chief  
9 purpose of this work was the preparation of carbosilane  
10 rings and the polymeric byproduct was not characterized in  
11 detail nor was its use as a SiC precursor suggested.  
12 Studies of this material indicate that it has an  
13 unacceptably low ceramic yield on pyrolysis. These polymers  
14 are related to those described in the instant process and  
15 are obtained by a similar procedure, however, they contain  
16 twice the required amount carbon necessary for  
17 stoichiometric silicon carbide and their use as SiC  
18 precursors was not suggested. Moreover, the starting

1 material, chloromethyl-dichloro-methylsilane, contains only  
2 two sites on the Si atom for chain growth and therefore  
3 cannot yield a structure which contains .tbd.SiCH.sub.2 --  
4 chain units. On this basis, the structure of the polymer  
5 obtained, as well as its physical properties and pyrolysis  
6 characteristics, must be significantly different from that  
7 of the subject process.

8 U. S. Patent No. 4,631,179 teaches a polymer which is  
9 a product of the ring-opening polymerization of (SiH.sub.2  
10 CH.sub.2).sub.2 also has the nominal composition "SiH.sub.2  
11 CH.sub.2 ". However, the actual structure of this polymer  
12 is fundamentally and functionally different from that of the  
13 instant process. Instead of a highly branched structure  
14 comprised of SiR.sub.3 CH.sub.2 --, --SiR.sub.2 CH.sub.2 --,  
15 .dbd.SiRCH.sub.2 --, and .tbd.SiCH.sub.2 -- units, the Smith  
16 polymer is reported to be a linear polycarbosilane which  
17 presumably has only [SiH.sub.2 CH.sub.2 ] as the internal  
18 chain segments. Such a fundamental structural difference

1 would be expected to lead to quite different physical and  
2 chemical properties. The fundamental difference in these  
3 two structures has been verified by the preparation of a  
4 linear polymer analogous to polymer and the comparison of  
5 its infrared and H-NMR spectra.

6 Another important difference between the process of  
7 Smith and the instant process is the method used to obtain  
8 the product polymer and the nature of the starting  
9 materials. The [SiH<sub>2</sub>CH<sub>2</sub>]<sub>2</sub> monomer used by  
10 Smith is difficult and expensive to prepare and not  
11 generally available, whereas the chlorocarbosilanes used in  
12 the instant process are readily available through commercial  
13 sources.

14 U. S. Patent No. 4,923,716 teaches chemical vapor  
15 deposition of silicon carbide which uses a "single  
16 molecular species" and which provides reactive fragments  
17 containing both silicon and carbon atoms in equal number  
18 this process. Linear and cyclic structures of up to six

1 units are mentioned. These compounds, which include both  
2 silanes and carbosilanes, are specifically chosen to be  
3 volatile for chemical vapor deposition use, and are  
4 distinctly different from the instant process, where the  
5 products are polymers of sufficiently high molecular weight  
6 that they cross-link before significant volatilization  
7 occurs. Such volatility would be highly undesirable for the  
8 applications under consideration for the polymers of the  
9 instant process, where excessive loss of the silicon-  
10 containing compound by vaporization on heating would be  
11 unacceptable.

12 The inventors hereby incorporate the above-referenced  
13 patents and articles into this application.

14 SUMMARY OF THE INVENTION

15 The present invention is generally directed to a  
16 process of forming a photo-curable pre-ceramic polymer for  
17 use in for fabricating ceramic matrix composites.

18 In a first separate aspect of the invention the process

1 includes the steps to silicon carbide ceramic.

2 In a second separate aspect of the invention the  
3 process includes the steps of reacting sodium acetylide with  
4 organo-chlorosilanes and condensing (polymerizing) the  
5 resultant organo-(ethynyl)-chloro silane product of step a  
6 with an excess of an alkali metal. The process includes  
7 the steps preparing a solution of thermoplastic photo-  
8 curable pre-ceramic polymer, passing a fiber, tape or fabric  
9 through the solution of thermoplastic photo-curable pre-  
10 ceramic polymer, applying the pre-preg to a shaped mandrel,  
11 using light energy to induce cross-linking of the photo-  
12 curable pre-ceramic polymer after application to the  
13 mandrel. The thermoplastic pre-ceramic polymer is cured and  
14 pyrolyzing the cured thermoplastic pre-ceramic polymer  
15 matrix composite material.

16 In a third separate aspect of the invention a  
17 single-step process for fabricating continuous ceramic fiber  
18 ceramic matrix composites employs a thermoplastic photo-

1 curable pre-ceramic polymer in which the component is shaped  
2 by a variety of standard composite fabrication techniques,  
3 such as filament winding, tape winding, and woven cloth  
4 winding. The process includes steps of passing ceramic  
5 fiber monofilament, tow, mat, or woven cloth through a  
6 solution of the thermoplastic photo-curable pre-ceramic  
7 polymer, applying ceramic fiber monofilament, tow, mat, or  
8 woven cloth to a shaped mandrel, using photo-energy of the  
9 ultraviolet, visible or infrared light spectrum to induce  
10 cross-linking (curing) of the photo-curable pre-ceramic  
11 polymer after application to the mandrel and either  
12 partially or completely pyrolyzing the now cured pre-ceramic  
13 polymer matrix composite material.

14 Other aspects and many of the attendant advantages will  
15 be more readily appreciated as the same becomes better  
16 understood by reference to the following detailed  
17 description.

18 The features of the present invention which are

1 believed to be novel are set forth with particularity in the  
2 appended claims.

3 DESCRIPTION OF DRAWINGS

4 Fig. 1 is schematic drawing of an apparatus for making  
5 flat plates of ceramic composites from photo-curable pre-  
6 ceramic polymers.

7 Fig. 2 is a photograph of the apparatus for making flat  
8 plates of Fig. 1.

9 Fig. 3 is schematic drawing of an apparatus for making  
10 cylinders of ceramic composites from photo-curable pre-  
11 ceramic polymers.

12 Fig. 4 is a photograph of the apparatus for making  
13 cylinders of Fig. 3.

14 Fig. 5 is a photograph of a photo-cured pre-ceramic  
15 polymer matrix coupon according to the present invention.

16 Fig. 6 is a SEM Photomicrograph at 35X of a fired SiC  
17 matrix test coupon prepared from a photo-cured pre-ceramic  
18 PECS polymer.

1       Fig. 7 is a SEM Photomicrograph at 350X of a fired SiC  
2 matrix test coupon prepared from photo-cured pre-ceramic  
3 PECS polymer.

4       Fig. 8 is a SEM Photomicrograph at 1500X of a fired SiC  
5 matrix test coupon prepared from photo-cured pre-ceramic  
6 PECS polymer.

7       DESCRIPTION OF THE PREFERRED EMBODIMENT

8       A continuous single step manufacturing process for  
9 fabricates dense low-porosity composites using novel cross-  
10 linkable pre-ceramic polymers and simple plastic industry  
11 technology adapted to the thermoset capability of the pre-  
12 ceramic polymer. The process eliminates the multi-cycle  
13 polymer impregnation pyrolysis method. The process is a  
14 simple controllable production process for fiber reinforced  
15 ceramic matrix composites, which can be easily automated  
16 into large manufacturing continuous processes. This process  
17 combines high-yield cross-linkable pre-ceramic polymers and  
18 a single step automated process mechanism to produce ceramic

1 components on the scale of aircraft fuselages, boat hulls,  
2 and large single ceramic sheets for space vehicle skin  
3 panels. The process provides chemically modified pre-  
4 ceramic polymers which are very fluid at temperatures 60° C-  
5 100° C, have high ceramic yields by weight of 75-95%,  
6 exhibit high purity and can be crosslinked into a thermoset  
7 with ultraviolet radiation. The process achieves by a  
8 series of chemical substitutions using commercially  
9 available polymers to incorporate ethynyl side groups on the  
10 polymers, which then contain unstable carbon triple bonds  
11 and cross-link, by hydrosilylation with Si-H groups upon  
12 photo-exposure. The process is to use the chemical  
13 substitution ethynyl side group chemistry to produce SiC,  
14 Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>N<sub>4</sub> and TiC upon pyrolysis after photo-  
15 exposure. Conversion of precursor polymers like  
16 polycarbosilane and polysilazane to poly(ethynyl)-  
17 carbosilane and poly(ethynyl)silazane achieve this  
18 objective. The process draws a fiber, tape, fabric, woven

1 cloth onto a mandrel or suitable substrate by first passing  
2 it through the chemically modified pre-ceramic polymer. The  
3 objective of this process is to saturate the fiber, tape,  
4 fabric, woven cloth with the very fluid pre-ceramic polymer  
5 and then photo-cure it on the mandrel or substrate as the  
6 saturated material is drawn along by motorized winding or  
7 pulling mechanisms known to the prior art. The process  
8 provides a continuous fabrication process to enable making a  
9 dense (total porosity <8%) fiber reinforced ceramic  
10 composite in a single step. This objective is achieved by  
11 compacting each layer of pre-ceramic polymer saturated  
12 material onto the already pyrolyzed layer below permitting  
13 excess polymer to impregnate this layer. The back-fill  
14 allowed here reduces the final component porosity, increases  
15 strength and provides a short path for volatiles to escape  
16 mitigating interlayer delamination. This layer by layer  
17 buildup is continued until the required component thickness  
18 is reached.

1       The novel nature of the photocurable pre-ceramic  
2 polymer enables a process, which is unique to porous filters  
3 not achievable with conventional pre-ceramic polymers. This  
4 process employs the ability to thermoset the pre-ceramic  
5 polymer into a rubbery hard solid prior to heating. In this  
6 form the pre-ceramic polymer can be heated and subsequently  
7 pyrolyzed without flowing into unwanted areas of the filter.  
8 Because of the ability of this process to produce high yield  
9 beta-SiC in near Si-C stoichiometry a matrix or coating is  
10 formed upon sintering that is highly receptive to heating  
11 with microwave energy. The microwave susceptible porous  
12 filter is ideally suited for trapping particulate from  
13 diesel engine exhausts and can be regeneratively used by  
14 microwave heating to a temperature above the oxidation  
15 threshold of the trapped particulate soot. The pre ceramic  
16 polymer can be made to form not only SiC but also other  
17 ceramic bodies such as  $\text{Si}_3\text{N}_4$ , BC, LAS, etc.

18       Referring to Fig. 1 in conjunction with Fig. 2 an

1 apparatus 10 for making flat plates of ceramic composites  
2 from photo-curable pre-ceramic polymers includes a frame 11  
3 with a process bed, a set of fabric rollers 12, a set of  
4 guide rollers 13, a set of drive rollers 14, a drive motor  
5 15, a compression roller 16, a process head 17 having a  
6 light-emitting lamp, a furnace 18, a covering 19 and a  
7 source of inert gas and a control panel 20. The source of  
8 inert gas provides an inert atmosphere.

9 Referring to Fig. 3 in conjunction with Fig. 4 an  
10 apparatus 110 for making cylinders of ceramic composites  
11 from photo-curable pre-ceramic polymers includes a dry  
12 nitrogen environmental chamber 111, a fabric roller 112, an  
13 applicator 113 of a photo-curable pre-ceramic polymer, a  
14 take-up mandrel 114, a pressure loaded compaction roller  
15 115, a light-emitting lamp 116 and a consolidation and  
16 pyrolysis zone 117. The consolidation and pyrolysis zone  
17 117 has a heater 118. The fabric roller dispenses woven  
18 ceramic fabric.

1           Commercially available polycarbosilanes and  
2       polycarbosiloxane polymers could be rendered photo-curable,  
3       by high intensity photo-radiation, through the addition of  
4       ethynyl side groups to the polymer. The polymer,  
5       poly(ethynyl) carbosilane, is rendered into an infusible  
6       thermoset upon photo-radiation. The process is able to  
7       similarly elevate ceramic yields to ~85 % by weight.

8           It has been demonstrated that various combinations of  
9       di-functional and tri-functional silane precursors can be  
10      utilized to enhance cross-linking and elevate ceramic yield.  
11      Combinations of dichlorodimethylsilane (di-functional) and  
12      trichlorophenylsilane (tri-functional) can be employed.  
13      Through the addition of branching, or cross-linking, ceramic  
14      yields as high as 77% have been obtained. Further, it is  
15      possible to doped these polymers, with boron for example, to  
16      control sintering and crystallization behavior.

17           While this process allows the addition of ethynyl side  
18      groups to potentially a wide range of available pre-ceramic

1 polymers, there are other methods of directly synthesizing  
2 poly(ethynyl)carbosilane, which are outlined below. In both  
3 of the following reaction paths, tri-functional organotri-  
4 chlorosilanes are utilized, in part or in entirety, to  
5 permit the introduction of photo-polymerizable side-groups,  
6 such as ethynyl groups derived from the reaction of sodium  
7 acetylide with chlorosilane.

8 In the first reaction route, sodium acetylide is  
9 reacted with the organotrichlorosilane, such as a methyl- or  
10 phenyltrichlorosilane, as shown in step 1. Typically, this  
11 is performed in a solvent, such as hexane or methylene  
12 chloride. The by-product of this reaction is sodium  
13 chloride, which is insoluble and can be easily removed by  
14 filtration and/or sedimentation (step 2). The resulting  
15 organo(ethynyl)chlorosilane can be reacted directly with  
16 sodium which is a Würtz type condensation reaction or mixed  
17 with an organodichlorosilane prior to the initiation of  
18 polycondensation. Assuming that all "R"s are the same, and

- 1 "a + b = 1", then the following reaction path can be  
 2 proposed:

Processing Step	Reaction
1. The addition of ethynyl (acetylide) side groups to tri-functional polysilazane reactant.	$a \{RSiCl_3 + g NaC\equiv CH \rightarrow RSiCl_{(3-g)}C\equiv CH_g + g NaCl\}$
2. Remove NaCl by filtration.	- ag NaCl
3. The addition of di-functional chain former (optional).	+ b {R <sub>2</sub> SiCl <sub>2</sub> }
4. Condensation of modified precursor solution to produce poly(ethynyl)silazane	$a(RSiCl_{(3-g)}C\equiv CH_g) + b(R_2SiCl_2) + 2[a(3-g) + b]Na \rightarrow 1/n\{Si_{(a+b)}R_{(a+2b)}C\equiv CH_{ag}\}_n + 2[a(3-g) + b]NaCl$

pre-ceramic polymer through the addition of sodium.	
---	--

Table 1: New processing route 1: Steps and reaction

chemistries to form poly(ethynyl)carbosilane-- Final Product  
 $= 1/n\{SiR_{(a+2b)}C\equiv CH_{ag}\}_n.$

1        In route 1, the photo-cross-linkable ethynyl group  
2        (acetylide) is added prior to the initiation of Würtz type  
3        condensation reaction. In route 2, a method of adding  
4        ethynyl side-groups post-condensation, thereby avoiding the  
5        exposure of the ethynyl ligand to sodium during the pre-  
6        ceramic polymer synthesis is disclosed. In this process,  
7        tri-functional and/or a mixture of di-functional and tri-  
8        functional chlorosilanes are reacted with a sub-  
9        stoichiometric quantity of metallic sodium, sufficient to  
10      bring about an increase in molecular weight and viscosity of  
11      the now pre-ceramic polymer backbone, but leaving a fraction  
12      of the chlorosilane reaction sites unreacted. The resulting

1 sodium chloride by-product can be removed by filtration  
2 and/or sedimentation (step 2).

3 Following polymer condensation, with unreacted  
4 chlorosilane sites intact, excess sodium acetylide is added  
5 to react with the aforementioned unreacted sites to produce  
6 poly(ethynyl)carbosilane photo-curable pre-ceramic polymer.  
7 The poly(ethynyl)carbosilane pre-ceramic polymer can be  
8 retrieved by solvent evaporation by the application of heat  
9 and/or in vacuo. Assuming that all "R"s are the same, and  
10 "a + b = 1", the final desired reaction product is expressed  
11 in the reaction path below in Table 2.

12 Table 2: New processing route 2: Steps, and reaction  
13 chemistries, to form poly(ethynyl)carbosilane.

Processing Step	Reaction
1. Mixture of di-functional and tri-functional	$a(RsiCl_3) + b(R_2SiCl_2) + [y/(3a+2b)]Na \rightarrow$ $(1/n)\{Si_{(a+b)}R_{(a+2b)}Cl_{[(1-y)/(3a+2b)]}\}_n +$ $[y/(3a+2b)] NaCl$

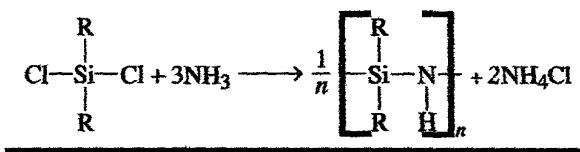
<p>chlorosilanes reacted with a sub- stoichiometric amount of sodium (where <math>y &lt; [3a+2b]</math>).</p>	
<p>2. Remove NaCl by filtration and/or sedimentation.</p>	$- [y / (3a+2b)] \text{ NaCl}$
<p>3. Addition of ethynyl side groups to partially condensed polysilazane polymer through the addition of excess sodium acetylide.</p>	$(1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{Cl}_{[(1-y)/(3a+2b)]} \}_n + [(1-y)/(3a+2b)] \text{NaC}\equiv\text{CH} \rightarrow$ $(1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n + [(1-y)/(3a+2b)] \text{NaCl}$

Product =  $(1/n) \{ \text{SiR}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n$ .

- 1 In the previous section, the method of preparing
- 2 poly(ethynyl)carbosilane, a photo-curable pre-ceramic

1 polymer precursor to silicon carbide has been reviewed. In  
2 this section, several of the promising methods of  
3 synthesizing polysilazane precursors to silicon nitride  
4 ( $\text{Si}_3\text{N}_4$ ) and a method of conversion to poly(ethynyl)silazane,  
5 a photo-curable pre-ceramic polymer precursor to high yield  
6  $\text{Si}_3\text{N}_4/\text{SiC}$  ceramic matrix composites are described.  $\text{Si}_3\text{N}_4$   
7 doped with 10-15 weight percent SiC has significantly lower  
8 creep at high temperature than pure  $\text{Si}_3\text{N}_4$ . The creep rate  
9 at the minimum was lower by a factor of three than that of  
10 the unreinforced, monolithic matrix of equal grain size.  
11 Thus, other researchers have recognized the potential  
12 importance of  $\text{Si}_3\text{N}_4/\text{SiC}$  nanocomposite matrices for  
13 continuous ceramic fiber reinforced composites used in high  
14 temperature applications. Two advantages of the process of  
15 the process are the ability to fabricate large-scale  
16 composites employing existing polymer composite fabrication  
17 techniques due to the addition of the photo-cross-linkable  
18 ethynyl side-groups and the inclusion of the carbon

1 containing ethynyl group should lead to the addition of  
2 approximately 5 to 20 weight percent SiC upon pyrolysis.  
3 One of the simplest and direct methods of preparing  
4 polysilazane precursors to silicon nitride, with a 70 weight  
5 percent ceramic yield is to dissolve dichlorosilane in  
6 dichloromethane to yield polysilazane oils. Pyrolysis in  
7 flowing nitrogen gas yielded nearly phase pure  $\alpha$ - $\text{Si}_3\text{N}_4$  after  
8 heat treatment at 1150°C for 12 hours. Numerous other  
9 permutations and refinements to the preparation of  
10 polysilazane oils and polymers have been developed. The  
11 reaction path of polysilazane formation using  
12 dichlorosilanes and ammonia is set out below:



13 A number of the most direct permutations include  
14 the use of trichlorosilanes, methyltrichlorosilanes,  
15 dimethyldichlorosilanes, and vinyl-, butyl-, phenyl-, ethyl-

1 , and hexyl- modified chlorosilanes. Increased molecular  
2 weight, and correspondingly increased ceramic yield, can be  
3 achieved by catalytically enhancing the cross-linking during  
4 final polymer preparation. A number of novel methods,  
5 including the use of ruthenium compounds and potassium  
6 hydride have been demonstrated to give ceramic yields upon  
7 pyrolysis as high as 85 percent. The inducement of cross-  
8 linking prior to pyrolysis is essential to achieving the  
9 high ceramic yields necessary to large-scale  
10 commercialization of  $\text{Si}_3\text{N}_4$  matrix composites for high  
11 temperature applications. The cross-linking methods cited  
12 in the literature, however, are chemical catalysts, making  
13 the shaping and forming processes extremely difficult.

14 A ceramic matrix of predominantly silicon nitride with  
15 about 10-15 % SiC by weight is nearly ideal for fabricating  
16 CMCs. In addition, the catalytic cross-linking of the  
17 polysilazane precursor dramatically increases ceramic yield.  
18 The synthesis route should produce high yield  $\text{Si}_3\text{N}_4/\text{SiC}$

1 nanocomposites employing a photocurable pre-ceramic polymer  
2 precursor.

3 One possible method would be to synthesize the  
4 unmodified polysilazane through the ammonolysis of various  
5 chlorosilane reactants in dichloromethane solvent followed  
6 by modifying the resulting polysilazanes, using a previously  
7 described process of chlorination followed by attachment of  
8 the ethynyl through reaction with sodium acetylide. Another  
9 alternative approach starts with a variety of dichloro-  
10 silanes and/or trichlorosilanes and reacts them with sodium  
11 acetylide at various concentrations, followed by ammonolysis  
12 to result in the final poly(ethynyl) silazane precursor as  
13 specifically detailed in the Table 3 below:

Processing Step	Reaction
1. addition of acetylide side groups trifunctional polysilazane reactant.	$a \{RSiCl_3 + g NaCCH \rightarrow RSiCl_{(3-g)}CCH_g + g NaCl\}$

2. remove NaCl by filtration	- g NaCl
2. addition of difunctional chain former	b {R <sub>2</sub> SiCl <sub>2</sub> }
3. ammonolysis of modified precursor solution to produce poly(ethynyl)silazane pre- ceramic polymer	a [RSiCl <sub>(3-g)</sub> CCH <sub>3</sub> ] + b [R <sub>2</sub> SiCl <sub>2</sub> ] + NH <sub>3</sub> $\rightarrow$ b{[SiR <sub>2</sub> (NH)] <sub>n</sub> } + a{[RSi(NH) <sub>(3-</sub> <sub>g</sub> )CCH <sub>3</sub> ] <sub>m</sub> } + 2[a(3-g) + 2b]NH <sub>4</sub> Cl

Table 3: Processing steps and reaction chemistries to form poly(ethynyl)silazane

1       The following are examples of combining commercially  
 2       available polymers and catalysts to achieve a final photo-  
 3       curable pre-ceramic polymer to SiC ceramics. In order to be  
 4       photo-curable, the polymer requires either double-bonded  
 5       carbons such as Allyl side groups or triple-bonded carbons  
 6       such as acetylide or propargyl side groups. The catalysts  
 7       can include a thermally curable component such as benzoil

- 1 peroxide and a photo-curable initiator such as Ciba-Geigy's  
 2 Irgacure 1800<sup>TM</sup> or a combination of camphorquinone and 2-  
 3 (dimethylamino)- ethyl methacrylate).

EXAMPLE 1

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoinitiator 2	None	None

EXAMPLE 2

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
RT initiator	N,N-dihydroxyparatoluidine	0.02

EXAMPLE 3

Category	Compound	Amount (grams)

Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.01
Photoinitiator 2	none	None

EXAMPLE 4

Category	Compound	Amount (grams)
Polymer	Poly(ethynyl)carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Ciba-Geigy's Irgacure 1800	0.02
Photoinitiator 2	none	None

EXAMPLE 5

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 6

Category	Compound	Amount

09294545-0123

		(grams)
Polymer	Poly(ethynyl) carbosilane	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 7

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	None
Photoinitiator 1	Camphorquinone	0.02
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate.	0.02

EXAMPLE 8

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	0.02
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

EXAMPLE 9

Category	Compound	Amount (grams)
Polymer	Allylhydridopolycarbosilane (5% allyl groups)	2.0
Catalyst	Benzoil Peroxide	none
Photoinitiator 1	Camphorquinone	0.01
Photoinitiator 2	2-(dimethylamino)ethyl methacrylate).	0.01

1        All of the above examples cross-linked under photo-  
 2        irradiation (using either ultraviolet light or blue light as  
 3        indicated) within a few minutes to an hour under continuous  
 4        irradiation at room temperature. The samples were  
 5        transformed by this method from thermoplastic to thermoset  
 6        pre-ceramic polymers which did not flow or deform  
 7        significantly upon subsequent heat-treatment and pyrolysis,  
 8        ultimately yielding SiC containing ceramics. The examples  
 9        are meant to be illustrative. A person trained in the art  
 10      can easily modify the ratios and selection of both pre-  
 11      ceramic polymer and/or photo-initiators and catalyst  
 12      combinations.

1        This process enables the continuous manufacture of  
2        fiber reinforced ceramic composites by the use of high  
3        ceramic yield pre-ceramic polymers which are photo-curable  
4        to a thermoset from a thermoplastic state. A composite in  
5        any form or shape is fabricated by photocuring each  
6        individual layer of fiber with in-situ pyrolysis of the pre-  
7        ceramic polymer impregnated into the fiber layer. The layer  
8        by layer of fiber, fabric or woven cloth is pressure loaded  
9        to press the thermoplastic polymer infiltrated fabric onto  
10      the mandrel or flat substrate thereby permitting excess  
11      polymer to impregnate the porous, already pyrolyzed, layer  
12      below. This single step process allows a shorter mean free  
13      path for volatiles to escape with less destruction than the  
14      removal of organics from more massive parts, for  
15      consolidation of each layer individually, and for increased  
16      layer to layer bonding and improved interlaminar shear  
17      strengths.

18        Silicon carbide (SiC) is one of several advanced

1 ceramic materials which are currently receiving considerable  
2 attention as electronic materials, as potential replacements  
3 for metals in engines, and for a variety of other  
4 applications where high strength, combined with low density  
5 and resistance to oxidation, corrosion and thermal  
6 degradation at temperatures in excess of 1000° C are  
7 required. Unfortunately, these extremely hard, non-melting  
8 ceramics are difficult to process by conventional forming,  
9 machining, or spinning applications rendering their use for  
10 many of these potential applications problematic. In  
11 particular, the production of thin films by solution  
12 casting, continuous fiber by solution or melt spinning, a  
13 SiC matrix composite by liquid phase infiltration, or a  
14 monolithic object using a precursor-based binder/sintering  
15 aid, all require a source of SiC which is suitable for  
16 solution or melt processing and which possesses certain  
17 requisite physical and chemical properties which are  
18 generally characteristic of polymeric materials.

1       Polymeric precursors to ceramics such as SiC afford a  
2 potential solution to this problem as they would allow the  
3 use of conventional processing operations prior to  
4 conversion to ceramic. A ceramic precursor should be  
5 soluble in organic solvents, moldable or spinnable,  
6 crosslinkable, and give pure ceramic product in high yield  
7 on pyrolysis. Unfortunately, it is difficult to achieve all  
8 these goals simultaneously. Currently available SiC  
9 precursor systems are lacking in one or more of these areas.  
10 Problems have been encountered in efforts to employ the  
11 existing polysilane and polycarbosilane precursors to SiC  
12 for preparation of SiC fiber and monolithic ceramic objects.  
13 All of these precursors have C/Si ratios considerably  
14 greater than one, and undergo a complex series of ill-  
15 defined thermal decomposition reactions which generally lead  
16 to incorporation of excess carbon. The existence of even  
17 small amounts of carbon at the grain boundaries within SiC  
18 ceramics has been found to have a detrimental effect on the

1 strength of the ceramic, contributing to the relatively low  
2 room-temperature tensile strengths typically observed for  
3 precursor-derived SiC fibers.

4 Efforts to develop polymeric precursors to SiC have  
5 focused largely on two types of polymers, polysilanes, which  
6 have a Si--Si backbone, and polycarbosilanes, in which the  
7 polymer backbone is [--Si--C--].<sub>n</sub>. The polysilanes all  
8 suffer from problems due to insolubility, infusibility  
9 and/or excess carbon incorporation. Certain of the  
10 polycarbosilanes have more suitable physical properties for  
11 processing; however, in general, these also contain a  
12 higher-than-1:1 C:Si ratio and incorporate excess carbon on  
13 pyrolysis.

14 In the case of the polycarbosilanes, high molecular  
15 weight linear polymers of the type [R.<sub>2</sub>SiCH<sub>2</sub>]<sub>n</sub>, where R is H and/or hydrocarbon groups, have been  
16 prepared by ring-opening-polymerization reactions starting  
17 from cyclic disilacyclobutanes using chloroplatinic acid and

1 related catalyst systems; however, such linear polycarbo-  
2 silanes generally exhibit low yields of ceramic product on  
3 pyrolysis due to chain "unzipping" reactions. For example,  
4 studies of high molecular weight [Me.<sub>2</sub>SiCH<sub>2</sub>.<sub>n</sub>]<sub>.sub.n</sub> polymers have indicated virtually complete  
5 volatilization on pyrolysis under an inert atmosphere to  
6 1000° C.

7         Use of propargyl groups (HC-=CCH<sub>2</sub>-), such as propargyl  
8 chloride (HC=CCH<sub>2</sub>Cl), propargyl bromide (HC= \_CCH<sub>2</sub>Br),  
9 propargyl alcohol (HC= \_CCH<sub>2</sub>OH), propargyl magnesium chloride  
10 (HC= \_CCH<sub>2</sub>MgCl), propargyl calcium chloride (HC= \_CCH<sub>2</sub>CaCl),  
11 propargyl arnine (HC= \_CCH<sub>2</sub>NH<sub>2</sub>), and other propargyl  
12 containing species introduces the photo-curable  
13 (Cross-linkable) triple-bonded carbon linkages into the pre-  
14 ceramic polymer.

15         U. S. Patent No. 5,153,295 teaches the use of ceramic  
16 polymers with an Si-C backbone structure, such as  
17 allylhydridopolycarbosilane (AHP-CS), formed from the

1 Grignard coupling reaction of a halomethylcarbosilane  
2 followed by reduction using a metal hydride in which either  
3 a UV cross-linkable ethynyl (i.e. acetylide) or propargyl.  
4 group has been introduced into the polymer by methodologies  
5 described previously.

6 The use of other ethynyl containing reagents, such as  
7 1-ethynyl-1 -cyclohexanol and 1,  
8 1'-ethynylene dicyclohexanol, can be directly coupled, due to  
9 the presence of hydroxyl (OH) bonds, to either halosilane  
10 (Si-X, where X= F, Cl, Br) and/or silanol (Si-OH) groups in  
11 the pre-ceramic polymer.

12 The use of benzoil peroxide or other chemical catalysts  
13 in conjunction with double or triple bonded carbon side  
14 groups within the pre-ceramic polymer to achieve  
15 crosslinking.

16 A single-step fabrication process of continuous ceramic  
17 fiber ceramic matrix composites employs a thermoplastic  
18 photo-curable pre-ceramic polymer in which the component is

1 shaped by a variety of standard composite fabrication  
2 techniques, such as filament winding, tape winding, and  
3 woven cloth winding. The process includes steps of  
4 passing ceramic fiber monofilament, tow, mat, or woven cloth  
5 through a solution of the thermoplastic photo-curable pre-  
6 ceramic polymer, applying ceramic fiber monofilament, tow,  
7 mat, or woven cloth to a moving flat substrate and using a  
8 heated or unheated compaction roller to press the  
9 thermoplastic pre-ceramic polymer coated ceramic fiber onto  
10 flat substrate. The process also includes the steps of  
11 using photo-light of the ultraviolet, visible, or infrared  
12 light spectrum to induce cross-linking (curing) of the  
13 photo-curable pre-ceramic polymer thereby rendering a  
14 thermoset polymer and either partially or completely  
15 pyrolyzing the now cured pre-ceramic polymer matrix coated  
16 ceramic fiber material. The pre-ceramic polymer  
17 poly(ethynyl)carbosilane yields silicon carbide upon  
18 pyrolysis. The pre-ceramic polymer may also yield oxide

1     ceramic such as aluminum oxide upon pyrolysis. Other photo-  
2     curable pre-ceramic polymers may yield silicon nitride,  
3     aluminum nitride and titanium carbide, for example.

4         A first process of forming a photo-curable pre-ceramic  
5     polymer, poly(ethynyl)-carbosilane to silicon carbide  
6     ceramic includes the steps of reacting sodium acetylide  
7     with organo-chlorosilanes and condensing (polymerizing) the  
8     resultant organo-(ethynyl)chlorosilane product of step a  
9     with an excess of an alkali metal. The organochlorosilane  
10    is selected from a group of one or more of the following:  
11    dichlorodimethylsilane, trichloro-phenylsilane (tri-  
12    functional), and methyltrichlor.

13         A second process of forming a photo-curable pre-ceramic  
14    polymer, poly(ethynyl)-carbosilane to silicon carbide  
15    ceramic includes the steps of reacting sodium acetylide  
16    with organochloro-silanes and condensing (polymerizing) the  
17    resultant organo(ethynyl)-chlorosilane product of step a  
18    with an excess of an alkali metal sodium.

1       A third process of forming a photo-curable pre-ceramic  
2   polymer, poly(ethynyl)-carbosilane, to silicon carbide  
3   ceramic includes the steps of reacting sodium acetylide with  
4   a mixture of organodichlorosilanes and organo-  
5   trichlorosilanes and condensing (polymerizing) the  
6   resultant organo(ethynyl)-chlorosilane product of step a  
7   with an excess of an alkali metal.

8       A fourth process of forming a photo-curable pre-ceramic  
9   polymer, poly(ethynyl)-carbosilane to silicon carbide  
10   ceramic includes the steps of reacting a sub-stoichiometric  
11   amount of an alkali metal with organochloro-silanes and  
12   reacting the partially polymerized polyorganochlorosilane  
13   with sodium acetylide. The organochlorosilane is selected  
14   from a group consisting of one or more of the following:  
15   dichlorodimethylsilane, trichlorophenylsilane (tri-  
16   functional) and methyltrichlorosilane.

17       A fifth process of forming a photo-curable pre-ceramic  
18   polymer, poly(ethynyl)-carbosilane to silicon carbide

1 ceramic includes the steps of reacting a sub-  
2 stoichiometric amount of sodium metal with  
3 organochlorosilanes and reacting the partially polymerized  
4 polyorganochlorosilane with sodium acetylide.

5 A sixth process of forming a photo-curable pre-ceramic  
6 polymer, poly(ethynyl)carbosilane to silicon carbide  
7 ceramic includes the steps of reacting a sub-stoichiometric  
8 amount of an alkali metal with a mixture of organodichloro-  
9 silanes and organotrichlorosilanes and reacting the  
10 partially polymerized polyorganochlorosilane with sodium  
11 acetylide.

12 A seventh process of forming a photo-curable pre-  
13 ceramic polymer, poly(ethynyl)silazane, to silicon nitride  
14 ceramic includes the steps of reacting sodium acetylide with  
15 organochlorosilanes and condensing (polymerizing) the  
16 resultant organo(ethynyl)chlorosilane product of step a with  
17 ammonia.

18 An eighth process of forming a photo-curable pre-

1 ceramic polymer, poly(ethynyl)-silazane to silicon nitride  
2 ceramic includes the steps of reacting sodium acetylide with  
3 organochlorosilanes and condensing (polymerizing) the  
4 resultant organo(ethynyl)-chlorosilane product of step a  
5 with ammonia.

6 A ninth process of forming a photo-curable pre-ceramic  
7 polymer, poly(ethynyl)silazane, to silicon nitride ceramic  
8 includes the steps of reacting sodium acetylide with a  
9 mixture of organodichlorosilanes and organotrichloro-silanes  
10 and condensing (polymerizing) the resultant organo(ethynyl)-  
11 chlorosilane product of step a with ammonia. The  
12 organochlorosilane is selected from a group consisting of  
13 one or more of the following: dichlorodimethylsilane,  
14 trichlorophenylsilane (tri-functional) and methyltrichloro-  
15 silane.

16 A tenth process of forming a photo-curable pre-ceramic  
17 polymer, poly(ethynyl)-silazane to silicon nitride ceramic  
18 includes the steps of reacting a sub-stoichiometric amount

1 of ammonia with organochlorosilanes and reacting the  
2 partially polymerized polyorganochlorosilazane with sodium  
3 acetylide.

4 An eleventh process of forming a photo-curable pre-  
5 ceramic polymer, poly(ethynyl)-silazane to silicon nitride  
6 ceramic includes the steps of reacting a sub-stoichiometric  
7 amount of ammonia with organochlorosilanes and reacting the  
8 partially polymerized polyorganochlorosilazane with sodium  
9 acetylide.

10 A twelfth process of forming a photo- curable pre-  
11 ceramic polymer, poly(ethynyl)-silazane to silicon nitride  
12 ceramic includes the steps of reacting a sub-stoichiometric  
13 amount of ammonia with with a mixture of organodichloro-  
14 silanes and organotrichlorosilanes and reacting the  
15 partially polymerized polyorganochlorosilazane with sodium  
16 acetylide.

17 A thirteen process for fabricating a ceramic matrix  
18 composites includes the steps of preparing a solution of

1 thermoplastic photo-curable pre-ceramic polymer, passing a  
2 pre-preg through the solution of thermoplastic photo-curable  
3 pre-ceramic polymer, applying the pre-preg to a shaped  
4 mandrel, using light energy to induce cross-linking of the  
5 photo-curable pre-ceramic polymer after application to the  
6 mandrel whereby the thermoplastic pre-ceramic polymer is  
7 curved and pyrolyzing the cured thermoplastic pre-ceramic  
8 polymer matrix composite material.

9 A process of forming a photo-curable pre-ceramic  
10 polymer, poly(ethynyl)-carbosilane to silicon carbide  
11 ceramic includes the steps of (a) reacting sodium acetylide  
12 with organo-chlorosilanes and (b) condensing (polymerizing)  
13 the resultant organo-(ethynyl)chlorosilane product of step a  
14 with an excess of an alkali metal. The organochlorosilane  
15 is selected from a group of one or more of the following:  
16 dichlorodimethylsilane, trichloro-phenylsilane (tri-  
17 functional) and methyltrichlorosilane.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)-carbosilane to silicon carbide  
2 ceramic includes the steps of (a) reacting sodium acetylide  
3 with organochloro-silanes and (b) condensing (polymerizing)  
4 the resultant organo(ethynyl)-chlorosilane product of step a  
5 with an excess of an alkali metal sodium. The rganochloro-  
6 silane is selected from a group consisiting of one or more  
7 of the following: dichlorodimethylsilane, trichlorophenyl-  
8 silane (tri-functional) and methyltrichlorosilane.

9 A process of forming a photo-curable pre-ceramic  
10 polymer, poly(ethynyl)-carbosilane, to silicon carbide  
11 ceramic includes the steps of (a) reacting sodium acetylide  
12 with a mixture of organodichlorosilanes and organotrichloro-  
13 silanes and (b) condensing (polymerizing) the resultant  
14 organo(ethynyl)-chlorosilane product of step a with an  
15 excess of an alkali metal.

16 A process of forming a photo-curable pre-ceramic  
17 polymer, poly(ethynyl)-carbosilane to silicon carbide  
18 ceramic includes the steps of (a) reacting a sub-

1 stoichiometric amount of an alkali metal with organochloro-  
2 silanes and (b) reacting the partially polymerized  
3 polyorganochlorosilane with sodium acetylide. The  
4 organochlorosilane is selected from a group consisting of  
5 one or more of the following: dichlorodimethylsilane,  
6 trichlorophenylsilane (tri-functional) and  
7 methyltrichlorosilane.

8 A process of forming a photo-curable pre-ceramic  
9 polymer, poly(ethynyl)- carbosilane to silicon carbide  
10 ceramic includes the steps of (a) reacting a sub-  
11 stoichiometric amount of sodium metal with organochloro-  
12 silanes and (b) reacting the partially polymerized  
13 polyorganochlorosilane with sodium acetylide. The  
14 organochlorosilane is selected from a group consisting of  
15 one or more of the following: dichlorodimethylsilane,  
16 trichlorophenylsilane (tri-functional) and methyltrichloro-  
17 silane.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)carbosilane to silicon carbide ceramic  
2 includes the steps of (a) reacting a sub-stoichiometric  
3 amount of an alkali metal with a mixture of organodichloro-  
4 silanes and organotrichlorosilanes and (b) reacting the  
5 partially polymerized polyorganochlorosilane with sodium  
6 acetylide.

7 A process of forming a photo-curable pre-ceramic  
8 polymer, poly(ethynyl)silazane, to silicon nitride ceramic  
9 includes the steps of (a) reacting sodium acetylide with  
10 organochlorosilanes and (b) condensing (polymerizing) the  
11 resultant organo(ethynyl)chloro-silane product of step a  
12 with ammonia. The organochlorosilane is selected from a  
13 group consisting of one or more of the following:  
14 dichlorodimethylsilane, trichlorophenylsilane (tri-  
15 functional) and methyltrichlorosilane

16 A process of forming a photo-curable pre-ceramic  
17 polymer, poly(ethynyl)-silazane to silicon nitride ceramic  
18 includes the steps of (a) reacting sodium acetylide with

1 organochlorosilanes and (b) condensing (polymerizing) the  
2 resultant organo(ethynyl) chloro-silane product of step a  
3 with ammonia. The organochlorosilane is selected from a  
4 group consisting of one or more of the following:  
5 dichlorodimethylsilane, trichlorophenylsilane (tri-  
6 functional) and methyltrichlorosilane

7 A process of forming a photo-curable pre-ceramic  
8 polymer, poly(ethynyl)silazane, to silicon nitride ceramic  
9 includes the steps of (a) reacting sodium acetylide with a  
10 mixture of organodichlorosilanes and organotrichlorosilanes  
11 and (b) condensing (polymerizing) the resultant organo-  
12 (ethynyl)chloro-silane product of step a with ammonia.

13 A process of forming a photo-curable pre-ceramic  
14 polymer, poly(ethynyl)silazane to silicon nitride ceramic  
15 includes the steps of (a) reacting a sub-stoichiometric  
16 amount of ammonia with organo-chlorosilanes and (b) reacting  
17 the partially polymerized polyorganochlorosilazane with  
18 sodium acetylide. The organochlorosilane is selected from a

1 group consisting of one or more of the following:  
2 dichlorodimethylsilane, trichlorophenylsilane (tri-  
3 functional) and methyltrichlorosilane  
4 A process of forming a photo-curable pre-ceramic  
5 polymer, poly(ethynyl)-silazane to silicon nitride ceramic  
6 includes the steps of (a) reacting a sub-stoichiometric  
7 amount of ammonia with organochlorosilanes and (b) reacting  
8 the partially polymerized polyorganochlorosilazane with  
9 sodium acetylide. The organochlorosilane is selected from a  
10 group consisting of one or more of the following:  
11 dichlorodimethylsilane, trichlorophenylsilane (tri-  
12 functional) and methyltrichlorosilane  
13 A process of forming a photo-curable pre-ceramic  
14 polymer, poly(ethynyl)-silazane to silicon nitride ceramic  
15 includes the steps of (a) reacting a sub-stoichiometric  
16 amount of ammonia with a mixture of organodichlorosilanes  
17 and organotrichlorosilanes and (b) reacting the partially  
18 polymerized polyorganochlorosilazane with sodium acetylide.

1           A process for fabricating a ceramic matrix composites  
2   includes the steps of (a) preparing a solution of  
3   thermoplastic photo-curable pre-ceramic polymer, (b) passing  
4   a pre-preg through the solution of thermoplastic photo-  
5   curable pre-ceramic polymer, (c) applying the pre-preg to a  
6   shaped mandrel, (d) using light energy to induce cross-  
7   linking of the photo-curable pre-ceramic polymer after  
8   application to the mandrel whereby the thermoplastic pre-  
9   ceramic polymer is curved and (e) pyrolyzing the cured  
10   thermoplastic pre-ceramic polymer matrix composite material.

11           A first single-step fabrication of continuous ceramic  
12   fiber ceramic matrix composites employing a thermoplastic  
13   photo-curable pre-ceramic polymer in which the component is  
14   shape by a variety of standard composite fabrication  
15   techniques, such as filament winding, tape winding, and  
16   woven cloth winding includes steps of (a) passing ceramic  
17   fiber monofilament, tow, mat, or woven cloth through a  
18   solution of the thermoplastic photo-curable pre-ceramic

1 polymer, (b) applying ceramic fiber monofilament, tow, mat,  
2 or woven cloth to a shaped mandrel, (c) using photo-energy  
3 of the ultraviolet, visible or infrared light spectrum to  
4 induce cross-linking (curing) of the photo-curable pre-  
5 ceramic polymer after application to the mandrel and (d)  
6 either partially or completely pyrolyzing the now cured pre-  
7 ceramic polymer matrix composite material. The pre-ceramic  
8 polymer is poly(ethynyl)carbosilane. The pre-ceramic  
9 polymer may yield silicon carbide upon pyrolysis. The pre-  
10 ceramic polymer may yield an oxide ceramic upon pyrolysis.  
11 The pre-ceramic polymer may yield titanium carbide upon  
12 pyrolysis. The pre-ceramic polymer may yield aluminum  
13 nitride upon pyrolysis. The pre-ceramic polymer may yield  
14 silicon nitride upon pyrolysis. The pre-ceramic polymer may  
15 yield aluminum oxide upon pyrolysis.

16 A second single-step fabrication of continuous ceramic  
17 fiber ceramic matrix composites employing a thermoplastic  
18 photo-curable pre-ceramic polymer in which the component is

1 shape by a variety of standard composite fabrication  
2 techniques, such as filament winding, tape winding, and  
3 woven cloth winding under inert atmosphere includes steps of  
4 (a) passing ceramic fiber monofilament, tow, mat, or woven  
5 cloth through a solution of the thermoplastic photo-curable  
6 pre-ceramic polymer, (b) applying ceramic fiber  
7 monofilament, tow, mat, or woven cloth to a shaped rotating  
8 mandrel, (c) use of a heated or unheated compaction roller  
9 to press the thermoplastic pre-ceramic polymer onto the  
10 mandrel, (d) using ultraviolet, visible, or infrared light  
11 to induce cross-linking (curing) of the photo-curable pre-  
12 ceramic polymer thereby rendering a thermoset polymer, (e)  
13 either partially or completely pyrolyzing the now cured pre-  
14 ceramic polymer matrix material and (f) followed by the  
15 final heat treatment of the shaped ceramic matrix composite  
16 "brown body". The pre-ceramic polymer is poly(ethynyl)carbo-  
17 silane. The pre-ceramic polymer may yield silicon carbide  
18 upon pyrolysis. The pre-ceramic polymer may yield an oxide

1     ceramic upon pyrolysis. The pre-ceramic polymer may yield  
2     titanium carbide upon pyrolysis. The pre-ceramic polymer  
3     may yield aluminum nitride upon pyrolysis. The pre-ceramic  
4     polymer may yield silicon nitride upon pyrolysis. The pre-  
5     ceramic polymer may yield aluminum oxide upon pyrolysis.

6                 A third single-step fabrication of continuous ceramic  
7     fiber ceramic matrix composites employing a thermoplastic  
8     photo-curable pre-ceramic polymer in which the component is  
9     shape by a variety of standard composite fabrication  
10    techniques, such as filament winding, tape winding, and  
11    woven cloth winding, includes steps of (a) passing ceramic  
12    fiber monofilament, tow, mat, or woven cloth through a  
13    solution of the thermoplastic photo-curable pre-ceramic  
14    polymer, (b) applying ceramic fiber monofilament, tow, mat,  
15    or woven cloth to a moving flat substrate, (c) using a  
16    compaction roller to press the thermoplastic pre-ceramic  
17    polymer coated ceramic fiber onto flat substrate, (d) using  
18    photo-light of the ultraviolet, visible, or infrared light

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1 spectrum to induce cross-linking (curing) of the  
2 photo-curable pre-ceramic polymer thereby rendering a  
3 thermoset polymer and (e) either partially or completely  
4 pyrolyzing the now cured pre-ceramic polymer matrix coated  
5 ceramic fiber material. ". The pre-ceramic polymer is  
6 poly(ethynyl)carbosilane. The pre-ceramic polymer may yield  
7 silicon carbide upon pyrolysis. The pre-ceramic polymer may  
8 yield an oxide ceramic upon pyrolysis. The pre-ceramic  
9 polymer may yield titanium carbide upon pyrolysis. The pre-  
10 ceramic polymer may yield aluminum nitride upon pyrolysis.  
11 The pre-ceramic polymer may yield silicon nitride upon  
12 pyrolysis. The pre-ceramic polymer may yield aluminum oxide  
13 upon pyrolysis.

14 Photocurable poly(ethynyl)carbosilane can be  
15 synthesized directly from difunctional and trifunctional  
16 chlorosilane reagents with the addition of sub-  
17 stoichiometric amounts of sodium to form poly(chloro)

1 silanes, followed by the addition of excess sodium acetylide  
2 to provide photocurable cross-linking sites.

3         Sodium metal suspension (40 % by weight) in oil was  
4 weighed. The suspension was washed three times in xylene and  
5 separated by centrifugation. The washed sodium was added to  
6 200 ml of xylene in the triple-neck reaction vessel. The  
7 refluxed reaction vessel was heated under flowing argon to  
8 100°C. The mixture of methylene bromide, dichlorodi-  
9 methylsilane, and trichlorophenyldisilane was slowly added  
10 using a burette. An exothermic reaction ensued and the  
11 temperature of reaction vessel contents reached 133oC and  
12 the mixture boiled vigorously under reflux for approximately  
13 30 minutes. The mixture was stirred for an additional hour  
14 while cooling. The dark purple/brown mixture, containing  
15 precipitates, was filtered and a clear yellow filtrate was  
16 obtained.

17         The resulting poly(chloro)carbosilane polymer was  
18 extracted from the filtrate by evaporation in a Rotovapor

1 apparatus. The resulting dark yellow viscous polymer was  
2 dissolved in tetrahydrofuran (THF). The appropriate amount  
3 of sodium acetylide powder was dissolved in dimethyl  
4 formamide (DMF) and added slowly to the poly(chloro)carbo-  
5 silane polymer solution and an exothermic reaction occurs  
6 and the color of the polymer solution turned a deep orange.  
7 Reaction byproducts were removed by filtration and the final  
8 poly(ethynyl)carbosilane polymer was obtained.

9 Six different examples of PECS, with varying ethynyl  
10 groups concentrations have been prepared as shown in Table 4  
11 Ethynyl concentration was varied from 0 to 25 percent (by  
12 mole).

13 In order to characterize the molecular weight and  
14 molecular weight distributions of polymers synthesized and  
15 utilized in this study, HPLC was utilized. A carefully  
16 prepared calibration curve was measured using NIST traceable  
17 molecular weight standards and measuring elution time. From  
18 this calibration curve, we were able to estimate the peak

- 1 molecular weight of the PECS synthesized based upon the  
 2 chromatograms.

**Table 4: Poly(ethynyl)carbosilane polymers synthesized in this study.**

Poly(ethynyl)carbosilane Synthesis Matrix											
Reactants	NAME	TRIAL 1			TRIAL 2			TRIAL 3			10% A/90% B
		MW	MOL	ML	GM	MOL	ML	GM	MOL	ML	
A	TCMS	149.48	0.0000	0.0000	0.000	0.0025	0.2936	0.374	0.0050	0.5871	0.747
B	DCMS	129.07	0.0500	6.0653	6.454	0.0475	5.7621	6.131	0.0450	5.4588	5.808
C	Methylene Bromide	173.85	0.0500	3.5093	8.693	0.0500	3.5093	8.693	0.0500	3.5093	8.693
D	NA	23	0.2000		4.600	0.2000		4.600	0.2000		4.600
E	NA ACETYLIDE	48	0.0000		0.000	0.0025		0.120	0.0050		0.240
D	40% Na-OIL				11.500			11.500			11.500
E	17.3% NA ACETYLIDE				0.000			0.694			1.387
TRIAL 4											
	NAME	15% A/85% B			20% A/80% B			25% A/75% B			TRIAL 6
		MW	MOL	ML	GM	MOL	ML	GM	MOL	ML	
A	TCMS	149.48	0.0075	0.8807	1.121	0.0100	1.1742	1.495	0.0125	1.4678	1.869
B	DCMS	129.07	0.0425	5.1555	5.485	0.0400	4.8523	5.163	0.0375	4.5490	4.840
C	Methylene Bromide	173.85	0.0500	3.5093	8.693	0.0500	3.5093	8.693	0.0500	3.5093	8.693
D	NA	23	0.2000		4.600	0.2000		4.600	0.2000		4.600
E	NA ACETYLIDE	48	0.0075		0.360	0.0100		0.480	0.0125		0.600
D	40% Na-OIL				11.500			11.500			11.500
E	17.3% NA ACETYLIDE				2.081			2.775			3.468

In Table 5 below, several of our polymers are compared with Dow Corning PCS. Our materials were purposely prepared as viscous fluids for greater ease in fabrication.

POLYMER	ELUTION TIME	MORPHOLOGY	MOLECULAR WEIGHT
Dow Corning PCS	14.468	Solid Flake	4400

PECS (0% ethynyl) A	16.598	Viscous Fluid	750
PECS (0% ethynyl) B	16.449	Viscous Fluid	700
PECS (5% ethynyl)	16.050	Viscous Fluid	1300
PECS (15% ethynyl)	16.862	Viscous Fluid	600
PECS (20% ethynyl) A	16.504	Viscous Fluid	700
PECS (20% ethynyl) B	15.973	Viscous Fluid	1400
PECS (25 % ethynyl)	16.732	Viscous Fluid	580

Table 5: Molecular Weights and HPLC Elution Times (peak) for PECS Synthesized by MATECH and Compared with Dow Corning PCS

1       One of the polymers synthesized as described above was  
 2       used to fabricate a ceramic matrix composite using woven  
 3       ceramic fabric. 7.0 grams of Poly(ethynyl)carbosilane with  
 4       15% ethynyl side-groups for cross-linking was impregnated  
 5       into 4 layers of woven ALTEX fabric. The resulting pre-preg  
 6       was photocured over night to produce cross-linked matrix and  
 7       then fired in Argon gas to 1200oC for one hour. The  
 8       resulting product was a ceramic coupon suitable for testing  
 9       and evaluation.

1       The polymer synthesized above, 7.0 grams of Poly  
2 (ethynyl)carbosilane with 15% ethynyl side-groups for cross-  
3 linking was impregnated into 4 layers of woven ALTEX fabric.  
4 The resulting pre-preg was photocured over night to produce  
5 cross-linked matrix and then fired in Argon gas to 1200oC  
6 for one hour. The resulting product was a ceramic coupon  
7 suitable for testing and evaluation.

8       The resulting SiC ceramic matrix composite (CMC) has  
9 been characterized. After only two processing cycles, the  
10 resulting CMC has an apparent density of 2.134 grams/cc and  
11 a porosity of 38.24 percent (%). In addition, it exhibits  
12 good strength and sounds very much like a ceramic when  
13 tapped. Scanning Electron Microscopy (SEM) photomicrographs  
14 reveal that the woven fiber tows (of approximately 500 mono-  
15 filaments each) are well bonded with minimal porosity, even  
16 at high magnification. Large pores are still present  
17 between tows, however, which can permit further  
18 densification through repeated polymer-impregnation-

1 pyrolysis (PIP) cycles.

2 EXAMPLE 10

3       For 25% ethynyl side-group substitution, 11.50 grams of  
4 sodium metal suspension (40 % sodium by weight) in oil was  
5 weighed. The suspension was washed three times in xylene and  
6 separated by centrifugation. The washed sodium was added to  
7 200 ml of xylene in the triple-neck reaction vessel. The  
8 refluxed reaction vessel was heated under flowing argon to  
9 100° C. A mixture of 8.693 grams methylene bromide, 4.840  
10 grams dichlorodimethylsilane, and 1.869 grams trichloro-  
11 phenylsilane was slowly added using a burette. An exothermic  
12 reaction ensued and the temperature of reaction vessel  
13 contents reached 133°C and the mixture boiled vigorously  
14 under reflux for approximately 30 minutes. The mixture was  
15 stirred for an additional hour while cooling. The dark  
16 purple/brown mixture, containing precipitates, was filtered  
17 and a clear yellow filtrate was obtained.

18       The resulting poly(chloro)carbosilane polymer was

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1 extracted from the filtrate by evaporation in a Rotovapor  
2 apparatus. The resulting dark yellow viscous polymer was  
3 dissolved in 50 ml tetrahydrofuran (THF). 0.600 grams of  
4 sodium acetylide powder was dissolved in 5.0 ml dimethyl  
5 formamide (DMF) and added slowly to the poly(chloro)carbo-  
6 silane polymer solution and an exothermic reaction occurred  
7 and the color of the polymer solution turned a deep purple-  
8 red. Reaction byproducts were removed by filtration and the  
9 final poly(ethynyl)carbosilane polymer dissolved in THF was  
10 obtained. The polymer was then extracted from the filtrate  
11 by evaporation in a Rotovapor apparatus, yielding  
12 approximately 8.0 grams of poly(ethynyl)carbosilane.

13 EXAMPLE 11

14 For 20% ethynyl side-group substitution, 11.50 grams of  
15 sodium metal suspension (40 % sodium by weight) in oil was  
16 weighed. The suspension was washed three times in xylene and  
17 separated by centrifugation. The washed sodium was added to  
18 200 ml of xylene in the triple-neck reaction vessel. The

1 refluxed reaction vessel was heated under flowing argon to  
2 100° C. A mixture of 8.693 grams methylene bromide, 5.163  
3 grams dichlorodimethylsilane, and 1.495 grams trichloro-  
4 phenylsilane was slowly added using a burette. An exothermic  
5 reaction ensued and the temperature of reaction vessel  
6 contents reached 133°C and the mixture boiled vigorously  
7 under reflux for approximately 30 minutes. The mixture was  
8 stirred for an additional hour while cooling. The dark  
9 purple/brown mixture, containing precipitates, was filtered  
10 and a clear yellow filtrate was obtained.

11 The resulting poly(chloro)carbosilane polymer was  
12 extracted from the filtrate by evaporation in a Rotovapor  
13 apparatus. The resulting dark yellow viscous polymer was  
14 dissolved in 50 ml tetrahydrofuran (THF). 0.480 grams of  
15 sodium acetylide powder was dissolved in 5.0 ml dimethyl  
16 formamide (DMF) and added slowly to the poly(chloro)-  
17 carbosilane polymer solution and an exothermic reaction  
18 occurred and the color of the polymer solution turned a deep

purple-red. Reaction byproducts were removed by filtration and the final poly(ethynyl)carbosilane polymer dissolved in THF was obtained. The polymer was then extracted from the filtrate by evaporation in a Rotovapor apparatus, yielding approximately 8.0 grams of poly(ethynyl)carbosilane.

EXAMPLE 12

For 15% ethynyl side-group substitution, 11.50 grams of sodium metal suspension (40 % sodium by weight) in oil was weighed. The suspension was washed three times in xylene and separated by centrifugation. The washed sodium was added to 200 ml of xylene in the triple-neck reaction vessel. The refluxed reaction vessel was heated under flowing argon to 100°C. A mixture of 8.693 grams methylene bromide, 5.485 grams dichlorodimethylsilane, and 1.121 grams trichlorophenylsilane was slowly added using a burette. An exothermic reaction ensued and the temperature of reaction vessel contents reached 133oC and the mixture boiled vigorously under reflux for approximately 30 minutes. The mixture was

1 stirred for an additional hour while cooling. The dark  
2 purple/brown mixture, containing precipitates, was filtered  
3 and a clear yellow filtrate was obtained.

4 The resulting poly(chloro)carbosilane polymer was  
5 extracted from the filtrate by evaporation in a Rotovapor  
6 apparatus. The resulting dark yellow viscous polymer was  
7 dissolved in 50 ml tetrahydrofuran (THF). 0.360 grams of  
8 sodium acetylide powder was dissolved in 5.0 ml dimethyl  
9 formamide (DMF) and added slowly to the poly(chloro)carbo-  
10 silane polymer solution and an exothermic reaction occurred  
11 and the color of the polymer solution turned a deep purple-  
12 red. Reaction byproducts were removed by filtration and the  
13 final poly(ethynyl)carbosilane polymer dissolved in THF was  
14 obtained. The polymer was then extracted from the filtrate  
15 by evaporation in a Rotovapor apparatus, yielding  
16 approximately 8.0 grams of poly(ethynyl)carbosilane.

17 EXAMPLE 13

18 For 10% ethynyl side-group substitution, 11.50 grams of

1     sodium metal suspension (40 % sodium by weight) in oil was  
2     weighed. The suspension was washed three times in xylene and  
3     separated by centrifugation. The washed sodium was added to  
4     200 ml of xylene in the triple-neck reaction vessel. The  
5     refluxed reaction vessel was heated under flowing argon to  
6     100°C. A mixture of 8.693 grams methylene bromide, 5.808  
7     grams dichlorodimethylsilane, and 0.747 grams trichloro-  
8     phenylsilane was slowly added using a burette. An  
9     exothermic reaction ensued and the temperature of reaction  
10    vessel contents reached 133°C and the mixture boiled  
11    vigorously under reflux for approximately 30 minutes. The  
12    mixture was stirred for an additional hour while cooling.  
13    The dark purple/brown mixture, containing precipitates, was  
14    filtered and a clear yellow filtrate was obtained.

15       The resulting poly(chloro)carbosilane polymer was  
16    extracted from the filtrate by evaporation in a Rotovapor  
17    apparatus. The resulting dark yellow viscous polymer was  
18    dissolved in 50 ml tetrahydrofuran (THF). 0.240 grams of

1 sodium acetylide powder was dissolved in 5.0 ml dimethyl  
2 formamide (DMF) and added slowly to the poly(chloro)-  
3 carbosilane polymer solution and an exothermic reaction  
4 occurred and the color of the polymer solution turned a deep  
5 purple-red. Reaction byproducts were removed by filtration  
6 and the final poly(ethynyl)carbosilane polymer dissolved in  
7 THF was obtained. The polymer was then extracted from the  
8 filtrate by evaporation in a Rotovapor apparatus, yielding  
9 approximately 8.0 grams of poly(ethynyl)carbosilane.

10 EXAMPLE 14

11 For 5% ethynyl side-group substitution, 11.50 grams of  
12 sodium metal suspension (40 % sodium by weight) in oil was  
13 weighed. The suspension was washed three times in xylene and  
14 separated by centrifugation. The washed sodium was added to  
15 200 ml of xylene in the triple-neck reaction vessel. The  
16 refluxed reaction vessel was heated under flowing argon to  
17 100°C. A mixture of 8.693 grams methylene bromide, 6.131  
18 grams dichlorodimethylsilane, and 0.374 grams trichloro-

1 phenylsilane was slowly added using a burette. An exothermic  
2 reaction ensued and the temperature of reaction vessel  
3 contents reached 133°C and the mixture boiled vigorously  
4 under reflux for approximately 30 minutes. The mixture was  
5 stirred for an additional hour while cooling. The dark  
6 purple/brown mixture, containing precipitates, was filtered  
7 and a clear yellow filtrate was obtained.

8 The resulting poly(chloro)carbosilane polymer was  
9 extracted from the filtrate by evaporation in a Rotovapor  
10 apparatus. The resulting dark yellow viscous polymer was  
11 dissolved in 50 ml tetrahydrofuran (THF). 0.120 grams of  
12 sodium acetylide powder was dissolved in 5.0 ml dimethyl  
13 formamide (DMF) and added slowly to the poly(chloro)-  
14 carbosilane polymer solution and an exothermic reaction  
15 occurred and the color of the polymer solution turned a deep  
16 purple-red. Reaction byproducts were removed by filtration  
17 and the final poly(ethynyl)carbosilane polymer dissolved in  
18 THF was obtained. The polymer was then extracted from the

1 filtrate by evaporation in a Rotovapor apparatus, yielding  
2 approximately 8.0 grams of poly(ethynyl)carbosilane.

3 EXAMPLE 15

4 For 0% ethynyl side-group substitution, 11.50 grams of  
5 sodium metal suspension (40 % sodium by weight) in oil was  
6 weighed. The suspension was washed three times in xylene and  
7 separated by centrifugation. The washed sodium was added to  
8 200 ml of xylene in the triple-neck reaction vessel. The  
9 refluxed reaction vessel was heated under flowing argon to  
10 100°C. A mixture of 8.693 grams methylene bromide, 6.454  
11 grams dichlorodimethylsilane was slowly added using a  
12 burette. An exothermic reaction ensued and the temperature  
13 of reaction vessel contents reached 133°C and the mixture  
14 boiled vigorously under reflux for approximately 30 minutes.  
15 The mixture was stirred for an additional hour while  
16 cooling. The dark purple/brown mixture, containing  
17 precipitates, was filtered and a clear yellow filtrate was  
18 obtained.

1       The resulting polycarbosilane polymer was extracted  
2   from the filtrate by evaporation in a Rotovapor apparatus  
3   yielding approximately 8.0 grams of polycarbosilane with no  
4   ethynyl side-groups.

5       It has been demonstrated that several commercially  
6   available preceramic polymers can be made photocurable. The  
7   preceramic polymer CERASETTM SZ inorganic polymer sold by  
8   Honeywell Advanced Composites, Inc., which is a silazane-  
9   based polymer, can be made photocurable to both UV and blue  
10   light through the addition of photoinitiators. Also, the  
11   preceramic polymer allylhydridopolycarbosilane (AHPCS)  
12   polymer manufactured by Starfire Systems, Inc. can be made  
13   photocurable to both UV and blue light through the addition  
14   of photoinitiators.

15   EXAMPLE 16

16       A UV light photocurable polysilazane was produced by  
17   mixing 2.00 grams of CERASETTM SZ inorganic polymer with  
18   0.50 grams of IRGACURE® 1800, manufactured by Ciba Specialty

1   Chemicals, dissolved in 0.50 ml tetrahydrofuran. The  
2   resulting yellow fluid, upon exposure to a high intensity UV  
3   lamp, became a stiff, rigid polymer within an hour. The  
4   resulting cross-linked polymer maintained its shape upon  
5   heating and pyrolysis to 1200oC in flowing argon gas. The  
6   ceramic yield of the pyrolyzed polymer was in excess of 80  
7   percent. A control sample, without the photoinitiator,  
8   remained fluid after in excess of 24 hours of continuous UV  
9   irradiation.

10   EXAMPLE 17

11         A blue light photocurable polysilazane was produced by  
12   mixing 2.00 grams of CERASETTM SZ inorganic polymer with  
13   0.50 grams of Camphorquinone, obtained from Aldrich Chemical  
14   Company, dissolved in 0.50 ml tetrahydrofuran. The resulting  
15   yellow fluid, upon exposure to a high intensity blue lamp,  
16   became a stiff, rigid polymer within an hour. The resulting  
17   cross-linked polymer maintained its shape upon heating and  
18   pyrolysis to 1200oC in flowing argon gas. The ceramic yield

1 of the pyrolyzed polymer was in excess of 80 percent. A  
2 control sample, without the photoinitiator, remained fluid  
3 after in excess of 24 hours of continuous blue light  
4 irradiation.

5 EXAMPLE 18

6 A UV light photocurable allylhydridocarbosilane was  
7 produced by mixing 2.00 grams of allylhydridocarbosilane  
8 (15% allylchloride) polymer with 0.50 grams of IRGACURE®  
9 1800, manufactured by Ciba Specialty Chemicals, dissolved in  
10 0.50 ml tetrahydrofuran. The resulting yellow fluid, upon  
11 exposure to a high intensity UV lamp, became a stiff, rigid  
12 polymer within an hour. The resulting cross-linked polymer  
13 maintained its shape upon heating and pyrolysis to 1200°C in  
14 flowing argon gas. The ceramic yield of the pyrolyzed  
15 polymer was in excess of 80 percent. A control sample,  
16 without the photoinitiator, remained fluid after in excess  
17 of 24 hours of continuous UV irradiation.

18 EXAMPLE 19

1       A blue light photocurable allylhydridocarbosilane was  
2 produced by mixing 2.00 grams of allylhydridocarbosilane  
3 (15% allylchloride) polymer with 0.50 grams of Camphor-  
4 quinone, obtained from Aldrich Chemical Company, dissolved  
5 in 0.50 ml tetrahydrofuran. The resulting yellow fluid,  
6 upon exposure to a high intensity blue lamp, became a stiff,  
7 rigid polymer within an hour. The resulting cross-linked  
8 polymer maintained its shape upon heating and pyrolysis to  
9 1200°C in flowing argon gas. The ceramic yield of the  
10 pyrolyzed polymer was in excess of 80 percent. A control  
11 sample, without the photoinitiator, remained fluid after in  
12 excess of 24 hours of continuous blue light irradiation.

13       From the foregoing it can be seen that processes of  
14 forming a photo-curable pre-ceramic polymer and their  
15 applications have been described.

16       Accordingly it is intended that the foregoing  
17 disclosure shall be considered only as an illustration of  
18 the principle of the present process.